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### A Photosensitive Polymer Having Benzoin Ether Side Chains: Poly( $\alpha$ -Methylolbenzoin Methyl Ether Acrylate)

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## **A Photosensitive Polymer Having Benzoin Ether Side Chains: Poly( $\alpha$ -Methylolbenzoin Methyl Ether Acrylate)**

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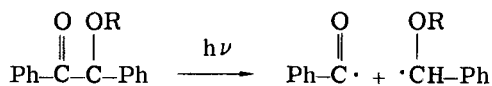
### ABSTRACT

Poly( $\alpha$ -methylolbenzoin methyl ether acrylate) and copolymers were prepared from a monomeric benzoin ether derivative,  $\alpha$ -methylolbenzoin methyl ether acrylate, and photopolymerizations and photoreactions of those polymers were studied. The photosensitive polymer having benzoin methyl ether side chains showed a greater efficiency in photoinitiating capabilities than nonpolymeric benzoin ether derivatives, such as benzoin, benzoin methyl ether,  $\alpha$ -methylbenzoin methyl ether, and benzoin methyl ether acetate. Gelation by the polymeric photoinitiators predominated in photopolymerizations with vinyl monomers.

### INTRODUCTION

Benzoin ether derivatives are widely used commercially. They are currently used in large amounts as photoinitiators for photocurable coatings, varnishes, printing inks, paints, etc. [1]. It has been known for a long time that benzoin and its derivatives, when exposed to UV light, produce polymerization-initiating radicals through Norrish Type I cleavage. In the case of benzoin alkyl ethers, benzoyl

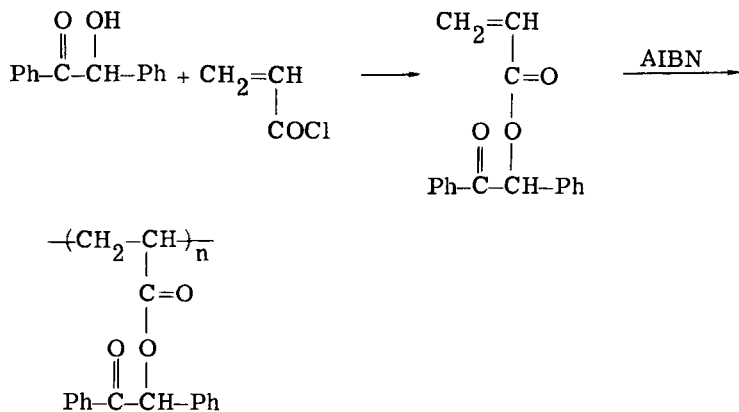
and  $\alpha$ -alkoxybenzyl radicals are produced by  $\alpha$ -cleavage, which initiates radical polymerization in the presence of reactive monomers [2, 3].



Benzoin alkyl ethers are known to be very effective photoinitiators, whereas benzoin itself has only relatively low reactivity [4].

Some photosensitive polymers containing photodissociable side-chains have had much attention recently. Neckers et al. [5, 6] have cited the studies on photosensitive polymers containing both a benzophenone functionality and a perester group, and they carried out photopolymerizations initiated by those polymers. Photopolymers containing sidechain benzophenone chromophores [7] and copolymers of photosensitive 3-oximino-2-butanone methacrylate [8] were also reported.

Poly(benzoin acrylate) is a photosensitive polymer containing side-chain benzoin moieties, and photoreactions of the polymer were investigated by Okawara et al. [9]. Poly(benzoin acrylate) was prepared by the polymerization of benzoin acrylate, which had been prepared by the reaction between benzoin and acryloyl chloride through ester formation.



Poly(benzoin acrylate) has also acted as a photoinitiator in the presence of vinyl monomers. However, benzoin ester derivatives are known to have very low reactivity in some photopolymerizations [10]. Hence, we tried to make some photosensitive polymers with higher reactivity in photoinitiation by incorporation of more photoreactive sidechain benzoin alkyl ethers.

In an earlier work we reported the synthesis and the photoreactions of photopolymers containing photosensitive  $\alpha$ -(2-carboxyethyl)benzoin

alkyl ethers [11]. In the present work we report a new photosensitive polymer containing photodissociable benzoin methyl ether moieties which are connected directly to the polymer backbone through the ester linkages of  $\alpha$ -methylolbenzoin methyl ether. Accordingly, the synthesis and photoreactions of polymeric benzoin methyl ether are discussed in this report.

## EXPERIMENTAL

### Chemicals and Instrumentation

Reagent-grade chemicals were purified by conventional procedures. Benzoin methyl ether was purchased from Aldrich Chemical Co. and used without further purification.

All measured temperatures were uncorrected. Melting points were measured by an Electrothermal Co. (England) capillary melting point apparatus. The inherent viscosities of the polymers obtained in chloroform at  $25 \pm 0.1^\circ\text{C}$  were determined with Cannon-Fenske capillary viscometer tubes.

IR spectra were taken on a JASCO Model A-102 infrared spectrophotometer. NMR spectra were obtained on a Varian T-60A spectrometer in ppm ( $\delta$  value) with TMS as internal standard. UV spectra were recorded on a Shimadzu Model UV-240 UV-visible recording spectrophotometer at concentrations of 0.1 and 1.0 mM for  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  transitions, respectively, at  $25^\circ\text{C}$ , and the molar absorptivity ( $\epsilon$ ) was calculated in L/(mol $\cdot$ cm). Thermal analysis was carried out with a Perkin-Elmer DSC-4 and a Shimadzu DT-30B instrument.

### $\alpha$ -Methylolbenzoin Methyl Ether (MBME)

$\alpha$ -Methylolbenzoin methyl ether was prepared according to the procedure of Hoffmann et al. [12] with some modification. Paraformaldehyde, 5.0 g (0.16 mol), was added to a stirred solution of benzoin methyl ether, 30.0 g (0.13 mol), in 200 mL DMSO containing 0.40 g KOH dissolved in 5 mL ethanol. The reaction was performed under nitrogen at  $40^\circ\text{C}$  for 3 h.

The reaction mixture was cooled to room temperature, neutralized with dilute hydrochloric acid, and then diluted to 120 mL by addition of a saturated sodium chloride solution. The mixture was extracted with ethyl acetate, and the extract was washed three times with a saturated sodium chloride solution and dried over anhydrous magnesium sulfate. The solution was concentrated under reduced pressure to give a pale yellow oil, which was crystallized slowly in a refrigerator. Colorless crystals of  $\alpha$ -methylolbenzoin methyl ether (MBME) were obtained by recrystallization from diethyl ether in a yield of 25.8 g (86.0%), mp  $70^\circ\text{C}$  (Ref. 12,  $72$ - $73^\circ\text{C}$ ); NMR(CDCl<sub>3</sub>): 8.1-7.9

(m, 2H, benzoyl), 7.6-7.2 (m, 8H, phenyl), 4.6-4.0 (two d, 2H,  $-\text{CH}_2\text{O}-$ ), 3.5 (s, 3H,  $-\text{O}-\text{CH}_3$ ); IR (KBr): 3300 ( $-\text{OH}$ ), 1680 (benzoyl  $\text{C}=\text{O}$ ), 1260 ( $-\text{O}-\text{CH}_3$ ), 1080 ( $-\text{CH}_2\text{O}-\text{H}$ )  $\text{cm}^{-1}$ ; UV ( $\lambda_{\text{max}}$  in tetrahydrofuran): 249 nm ( $\epsilon = 10100$ ), 343 nm ( $\epsilon = 150$ ).

$\alpha$ -Methylolbenzoin Methyl Ether Acrylate (BME Acrylate)

To a stirred solution of  $\alpha$ -methylolbenzoin methyl ether, 30.0 g (0.12 mol), and 24.0 mL of triethylamine in 120 mL of chloroform, acryloyl chloride, 75.0 g (0.83 mol) was added dropwise below  $10^\circ\text{C}$ . The reaction mixture was heated to  $40^\circ\text{C}$  for 2 h. The solvent was evaporated, and the residue was extracted with diethyl ether, washed with water, and dried over anhydrous magnesium sulfate. After stripping the solvent, a yellowish oil was obtained and crystallized from ethanol to give colorless crystals of BME acrylate in a yield of 26.1 g (87.0%), mp  $56^\circ\text{C}$ ; NMR ( $\text{CDCl}_3$ ): 8.0-7.8 (m, 2H, benzoyl), 7.5-7.2 (m, 8H, phenyl), 6.2-5.7 (m, 3H,  $-\text{CH}=\text{CH}_2$ ), 5.3-4.5 (two d, 2H,  $-\text{CH}_2\text{O}-$ ), 3.4 (s, 3H,  $-\text{O}-\text{CH}_3$ ); IR (KBr): 1730 ( $\text{CO}_2\text{R}$ ), 1678 (benzoyl  $\text{C}=\text{O}$ ), 1640 ( $\text{C}=\text{C}$ ), 1410 ( $=\text{CH}_2$  bending), 990 and 920 ( $\text{CH}=\text{CH}_2$ )  $\text{cm}^{-1}$ ; UV ( $\lambda_{\text{max}}$  in tetrahydrofuran): 250 nm, 340 nm ( $\epsilon = 224$ ).

$\alpha$ -Methylolbenzoin Methyl Ether Acetate (BME Acetate)

BME acetate was prepared by a reaction of  $\alpha$ -methylolbenzoin methyl ether and acetyl chloride. Yellowish crystals were obtained in a yield of 73.8%, mp  $55-57^\circ\text{C}$ ; NMR ( $\text{CDCl}_3$ ): 8.1-7.9 (m, 2H, benzoyl), 7.6-7.2 (m, 8H, phenyl), 5.1-4.5 (two d, 2H,  $-\text{CH}_2\text{O}-$ ), 3.35 (s, 3H,  $-\text{O}-\text{CH}_3$ ), 1.95 (s, 3H,  $\text{CH}_3-\text{COO}-$ ); IR (KBr): 1750 ( $\text{CO}_2\text{R}$ ), 1678 (benzoyl  $\text{C}=\text{O}$ ), 1240 (acetate band)  $\text{cm}^{-1}$ ; UV ( $\lambda_{\text{max}}$  in tetrahydrofuran): 252 nm ( $\epsilon = 15280$ ), 340 nm ( $\epsilon = 197$ ).

Polymerization and Copolymerization of BME Acrylate

All the polymerizations were carried out in degassed, sealed Pyrex ampules (inner diameter, 25 mm) covered with aluminum foil to protect them from light. Polymerization of BME acrylate was performed

TABLE 1. Results of Polymerization of BME Acrylate with AIBN at 60°C for 6 h

Polymer no.	BME acrylate, g	AIBN, mol%	Solvent, mL	Conversion, %	$\eta_{inh}^a$
PBM1	0.50	0.4	Dioxane (5.0)	96	0.18
PBM2	0.50	0.2	Dioxane (5.0)	76	0.13
PBM3	1.00	0.4	Benzene (1.5)	30	0.40
PBM4	3.00	0.2	Benzene (6.0)	79	0.41
PBA	<sup>b</sup>	1.9	Dioxane (5.0)	93	0.10

<sup>a</sup>The inherent viscosities were measured at 25°C at 0.5 g/dL in chloroform.

<sup>b</sup>PBA is poly(benzoin acrylate) obtained by polymerization of benzoin acrylate (0.50 g).

in 6.0 mL of benzene at 60°C for 6 h with AIBN as initiator. The results are summarized in Table 1.

The copolymers, poly(BME acrylate-co-styrene), were prepared by the polymerization of BME acrylate with styrene using AIBN (1.0 mol%). In a Pyrex ampule, the calculated amounts of BME acrylate were dissolved in styrene, and the combined weight was around 2 g. The ampule was sealed under vacuum, and the mixture was polymerized at 60°C for 6 h. The polymers were precipitated with excess methanol, and white powdery polymers were obtained. The copolymerization results are summarized in Table 2.

The compositions of BME acrylate in poly(BME acrylate-co-styrene) were calculated by determining the intensity ratios of IR absorption bands due to the carbonyl groups (1680  $\text{cm}^{-1}$ ) in BME acrylate units and the phenyl groups (1601  $\text{cm}^{-1}$ ). A working curve was plotted from the ratios of the absorbance at 1680 and 1601  $\text{cm}^{-1}$  of the mixtures of poly(BME acrylate) and polystyrene in potassium bromide pellets.

### Poly(Benzoin Acrylate)

Benzoin acrylate and poly(benzoin acrylate) were prepared according to the method of Okawara et al. [9]. Benzoin acrylate was obtained in 92% yield with mp 107°C (Ref. 9, 106°C). Benzoin acrylate was polymerized by AIBN (1.0 mol%) in dioxane at 60°C for 6 h.

TABLE 2. Results of Copolymerization of BME Acrylate with Styrene by 1.0 mol% AIBN in Bulk at 60°C for 6 h

Copolymer no.	BMEA in feed, mol%	Conversion, %	$\eta_{inh}^b$ , dL/g	BMEA in polymer, mol%
PBS1 <sup>c</sup>	50.0	64	0.14	29.4
PBS2	10.0	86	0.17	11.7
PBS3	1.0	96	0.26	1.0

<sup>a</sup>BMEA is  $\alpha$ -methylolbenzoin methyl ether acrylate (BME acrylate).

<sup>b</sup>Inherent viscosities measured at 20°C at 0.5 g/dL in chloroform.

<sup>c</sup>PBS1 was obtained by polymerization of BME acrylate with styrene in 3.0 mL of benzene.

### Photopolymerization

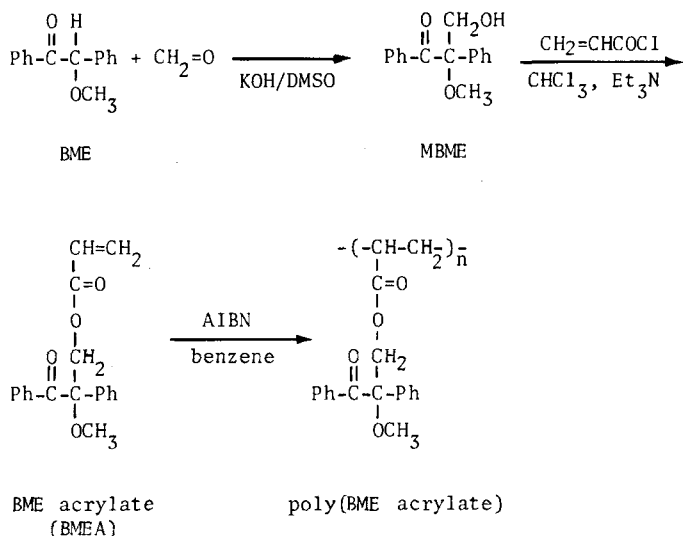
Photopolymerizations were carried out in Pyrex ampules containing styrene monomer and 1.0 mol% of photoinitiators such as benzoin, benzoin methyl ether,  $\alpha$ -methylolbenzoin methyl ether,  $\alpha$ -methylolbenzoin methyl ether acetate, poly(benzoin acrylate), and poly(BME acrylate). For the study of photopolymerization of copolymers, poly(BME acrylate-co-styrene), a solution of the copolymer and methyl methacrylate in benzene was UV-irradiated in a Pyrex ampule.

The ampules were degassed and sealed under vacuum by the freeze/thaw techniques. The sealed ampule was irradiated for a given time at 50 cm distance from the UV light source of 500 W high-pressure mercury lamp (Ushio Co., Japan) while rotating the ampule, where the light intensity was 58.6 mW/cm<sup>2</sup>. After the irradiation, the contents of the ampule were poured into an excess of methanol to precipitate the homopolymer and grafted or crosslinked polymers. In the photopolymerization of styrene initiated with poly(BME acrylate), intractable solid polymers were usually produced within 10 min irradiation when no solvents were used, and even gelation was observed with solvents after around 10 min irradiation.

## RESULTS AND DISCUSSION

### Synthesis of $\alpha$ -Methylolbenzoin Methyl Ether Acrylate (BME Acrylate)

$\alpha$ -Methylolbenzoin methyl ether (MBME) was prepared by reaction of benzoin methyl ether (BME) and paraformaldehyde according



SCHEME 1. Synthesis of poly(BME acrylate).

to a method similar to Hoffmann's patent [12]. From the reaction of MBME with acryloyl chloride, the monomeric  $\alpha$ -methylolbenzoin methyl ether acrylate (BME acrylate) was synthesized in 87% yield as shown in Scheme 1.

BME acrylate (BMEA) was confirmed by IR, NMR, and UV spectra. In a proton NMR spectrum, phenyl, vinyl, and methoxy protons are well identified. The characteristic IR absorption bands at  $1678 \text{ cm}^{-1}$  of carbonyl groups in benzoyl moieties, at  $1730 \text{ cm}^{-1}$  of ester groups, and at  $1640, 1410, 990, \text{ and } 920 \text{ cm}^{-1}$  of vinyl groups could be identified clearly.

### Polymerization and Copolymerization of BME Acrylate

The polymerizations of BME acrylate were accomplished with free-radical initiation in benzene or dioxane solution. The polymerization conditions and results are summarized in Table 1. The monomer, BME acrylate, was highly soluble in both benzene and methanol, and the polymers were obtained by precipitating into excess methanol as white powdery materials which did not form films. The polymers have higher viscosities when polymerized in benzene than in dioxane. The poly(BME acrylate) exhibited the characteristic IR absorption bands at  $1730 \text{ cm}^{-1}$  of ester groups and at  $1680 \text{ cm}^{-1}$  of carbonyl groups of benzoin methyl ether moieties. In the IR spectrum of the



poly(BME acrylate), only the vinyl absorption bands of the monomer disappeared.

The polymer PBM4 was used as a polymeric photoinitiator for the subsequent photopolymerizations. For the comparison of photoreactions, poly(benzoin acrylate) (PBA) was also prepared from benzoin acrylate according to the known procedure of Okawara et al. [9].

Benzoin ether derivatives (BME, MBME) and poly(BME acrylate), as well as benzoin and PBA, exhibited UV spectra corresponding to  $n-\pi^*$  transitions, as shown in Fig. 1. Poly(BME acrylate) showed ab-

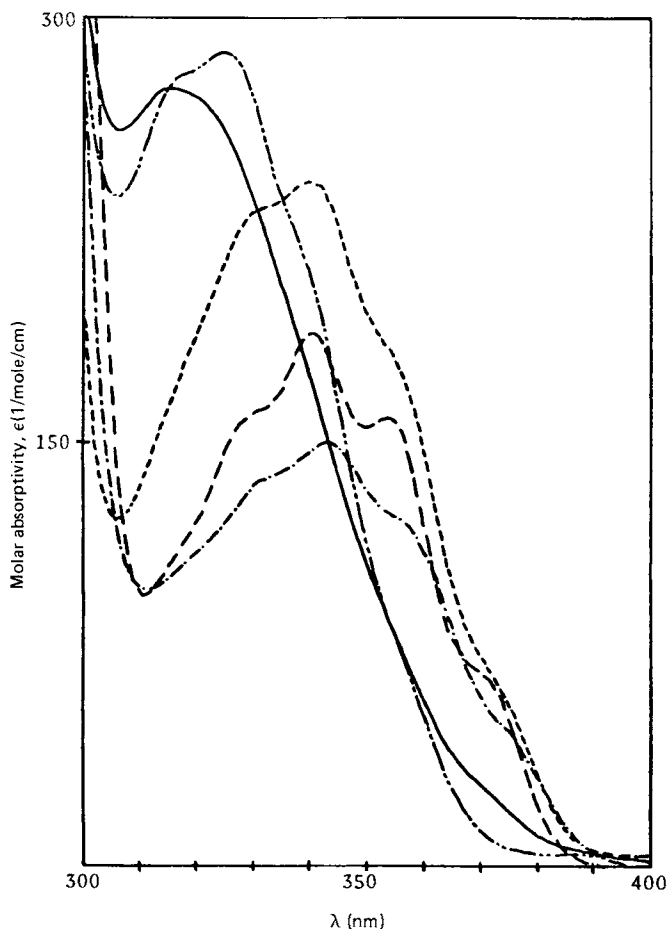


FIG. 1. UV absorption spectra of various photoinitiators of benzoin derivatives by  $n-\pi^*$  transition (1 mM in THF, 25°C): benzoin (—), PBA (- · - ·), poly(BME acrylate) (- - -), BME (- -), MBME (- · · -).

sorption maxima at 253 nm ( $\epsilon = 12560$ ) and 340 nm ( $\epsilon = 188$ ) in 1 mM THF solution.

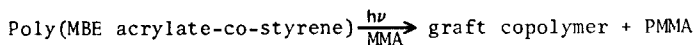
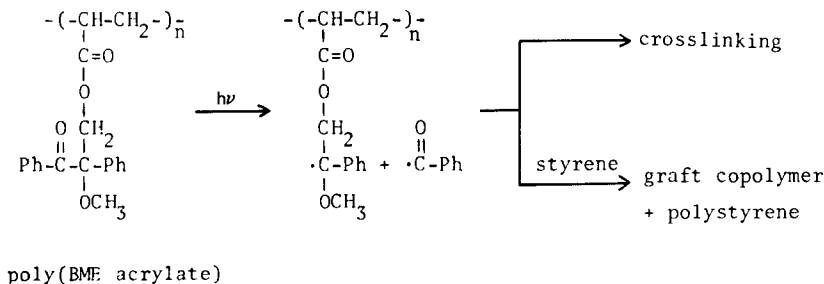
BME acrylate and styrene were copolymerized radically, and the results are shown in Table 2. Polymers PBS2 and PBS3 were made in bulk, but the polymer PBS1 was polymerized in benzene solution because BME acrylate is insoluble in styrene at those concentrations.

The compositions of BME acrylate in the copolymers were calculated from a working curve of ratios of IR absorbances at 1680 to that at 1601  $\text{cm}^{-1}$ . It is apparent that BME acrylate participates in chain transfer reactions to some extent. The lower the feed of BME acrylate contents, the higher the viscosity and the conversion.

Photopolymerization with Poly(BME Acrylate) as Photoinitiator

Upon UV irradiation of poly(BME acrylate), various photoreactions are possible with the benzoyl free radical and the polymer-bound  $\alpha$ -methoxybenzyl free radical, which are produced by photodecomposition of benzoin ether moieties as depicted in Scheme 2.

The photoinitiating capability of poly(BME acrylate) was compared with that of nonpolymeric photoinitiators such as benzoin, benzoin methyl ether,  $\alpha$ -methylolbenzoin methyl ether, and BME acetate. It was also tested as a polymeric photoinitiator compared to poly(benzoin acrylate) by polymerization with styrene. The total conversions to polystyrene initiated by two polymeric photoinitiators, poly(BME acrylate) and poly(benzoin acrylate), were much higher than those initiated by nonpolymeric photoinitiators, as shown in Fig. 2. The



SCHEME 2. Photoreaction and photopolymerization of poly(BME acrylate).

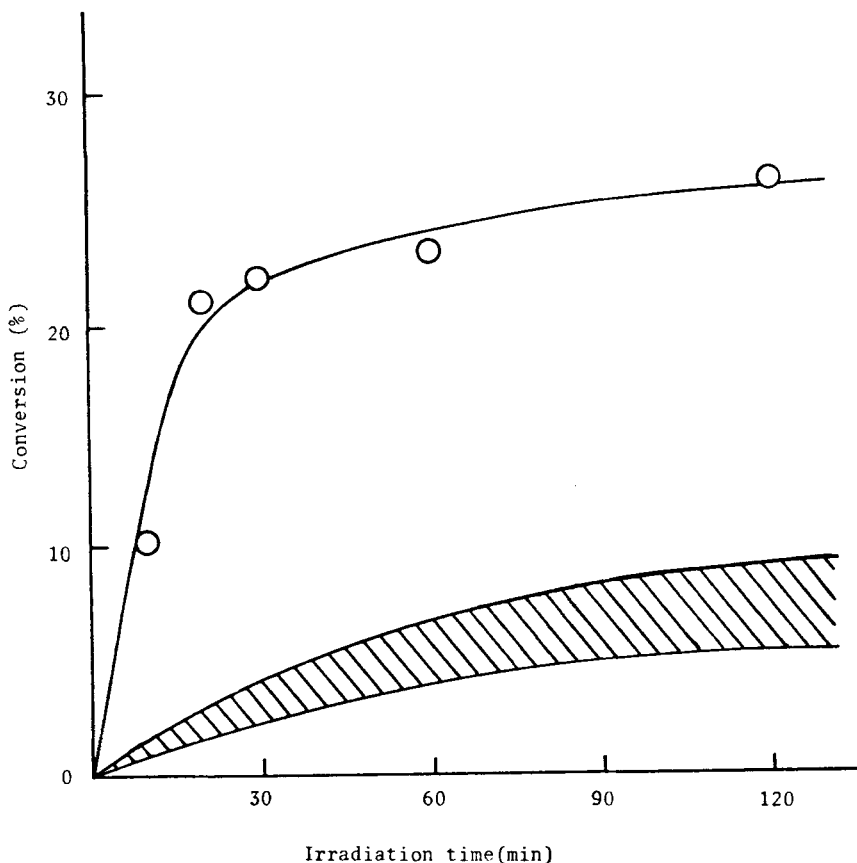


FIG. 2. Photopolymerization of styrene with various photoinitiators (1.0 mol%). poly(BME acrylate) (○), shaded area (benzoin, BME, MBME, BME acetate). Reaction conditions: styrene 3.0 g; benzene, 6.0 mL.

photoinitiators of benzoin derivatives gave less than 10% conversion in 2 h irradiation, whereas the polymeric photoinitiators gave higher than 20% in 1 h under the same reaction conditions. The higher conversion is partly ascribable to gel formation during polymerization, which protects the propagating free radical sites from termination. As a blank test of the photopolymerization, 5 mL of styrene was irradiated for 90 min, and only 0.08 g (1.6%) of rather low molecular weight polymers, considered to be negligible amounts in this study, were obtained. These results are very similar to Neckers' report [6].

TABLE 3. Methylene Chloride-Insoluble Fractions of Polystyrene Obtained by Photoinitiation with Poly(BME Acrylate)

Irradiation time, min	Methylene chloride-insoluble fraction
10	0.94
30	0.84
60	0.75
120	0.77

When poly(BME acrylate) was employed as a photoinitiator, gel formation was observed during the irradiation, while it was not observed in the case of monomeric initiators. Poly(BME acrylate)-initiated polystyrene was Soxhlet extracted overnight with methylene chloride, and the methylene chloride-insoluble fractions were measured, as shown in Table 3. The insoluble fractions were over 0.7. At higher conversion, the fraction was lower.

Neckers [6] explained that the large amounts of insoluble polymer fraction in his study were produced by hindered terminations of the radicals inside the polymer coils and formation of longer chains. However, the phenomena in this work are also due to the different characters of the benzoyl and the  $\alpha$ -methoxybenzyl radicals produced by cleavage of the benzoin methyl ether moieties by UV irradiation. There is a controversial question concerning the reactivity and the role of the two radical species produced from benzoin alkyl ethers in photopolymerization. Hageman [13, 14] asserted different reactivities and roles, whereas Pappas [3, 15] claimed the same reactivities for both radicals. Both research groups explained their theory with sound experimental evidence.

It was shown that the benzoyl radicals have a greater tendency to add to double bonds than  $\alpha$ -alkoxybenzyl radicals [14]. The benzoyl radical fragments usually participate in the initiation process, while the  $\alpha$ -methoxybenzyl radical fragments participate in the termination reaction in the presence of styrene monomers. It is unclear which theory is more plausible for the explanation of the results of this work. Norrish Type I cleavage of the benzoin methyl ether moieties in poly(BME acrylate) would give cleaved benzoyl radicals and polymer-bound  $\alpha$ -methoxybenzyl radicals. When the photodissociable BME groups are attached to a polymer backbone as in this study, it is easier to crosslink in the presence of reactive vinyl monomers, regardless of which theory is valid, because half the radicals produced are attached to polymer chains.

TABLE 4. Photopolymerization of Methyl Methacrylate by Poly(BME Acrylate-co-Styrene)<sup>a</sup>

Sample no.	BMEA <sup>b</sup> in copolymer, mol%	Conversion, %	PMMA, g/mmol BMEA
PBS1	29.4	44	7.6
PBS2	11.7	26	8.4
PBS3	1.0	6	11.5
PBMEA <sup>c</sup>	100	52	4.9
PMMA <sup>d</sup>	0	Negligible	-

<sup>a</sup>Photopolymerization condition: MMA, 5.00 g; copolymer, 0.15 g; benzene, 10 mL; time, 30 min.

<sup>b</sup>BMEA: BME acrylate.

<sup>c</sup>PBMEA. Poly(BME acrylate) homopolymer was used instead of the copolymer.

<sup>d</sup>Without the copolymers, 5.00 g of methyl methacrylate in benzene was irradiated for 30 min, and no polymers were obtained.

### Photoreaction of Copolymer

The copolymers of BME acrylate and styrene were irradiated in the presence of excess methyl methacrylate (MMA) in benzene, and graft and homopolymerization took place. Benzoin methyl ether moieties in the copolymers served as photoinitiating and grafting sites by UV irradiation. Large portions of the polymers obtained were insoluble in common solvents of poly(methyl methacrylate) (PMMA). The photoreactions of the copolymers with MMA are summarized in Table 4.

Conversions to PMMA were increased with increasing BME acrylate contents of the copolymers, as expected, while the amounts of PMMA formed per mmole of BME acrylate units gradually decreased with increasing BME acrylate content. When the content of BME acrylate is increased, the production of both radicals is high, but the chances of termination by coupling are also increased. These results are comparable to those in Okawara's work [9]. In the photopolymerization by these copolymers, polymers insoluble in acetone were obtained at over 70%, except polymer PBS3. The large amounts of insoluble polymers are also ascribable to the crosslinking of polymer-bound  $\alpha$ -methoxybenzyl radicals. By careful control of the BME acrylate contents of the copolymer chains, a useful photocurable polymer system can be designed.

## CONCLUSION

We have shown that new photosensitive polymers having benzoïn methyl ether sidechains can be made by homo- or copolymerization of  $\alpha$ -methylolbenzoïn methyl ether acrylate (BME acrylate). When employed as a polymeric photoinitiator in the photopolymerization of styrene, poly(BME acrylate) exhibited much higher photoreactivity compared with nonpolymeric photoinitiators such as benzoïn, benzoïn methyl ether, and  $\alpha$ -methylolbenzoïn methyl ether. Poly(BME acrylate-co-styrene) copolymers were also used in photopolymerization and photografting in the presence of vinyl monomers. The conversion and the degree of crosslinking of photopolymerization can be controlled by adjusting the benzoïn methyl ether side chains in the polymeric photoinitiators. The observed formation of large amounts of insoluble polymer in photopolymerizations is ascribable to the polymer-bound  $\alpha$ -methoxybenzyl radicals produced by cleavage of the benzoïn methyl ether moieties. This indicates that photosensitive polymers can be applied to photocurable polymer systems, and work on this is in progress.

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