

Photocrosslinking Reactions of Polyfunctional Monomers with Vinyl Ether or Propargyl Ether Groups

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SYNOPSIS

Photocrosslinking reactions of di(2-vinyloxy)ethyl ether of bisphenol-A (BPAEVE), dipropargyl ether of bisphenol-A (BPAPE), and diglycidyl ether of bisphenol-A (BPAGE) were carried out using various cationic photoinitiators in 1,2-dichloroethane. The reaction of BPAEVE occurred with high conversion to give the gel products, and the reaction rate of BPAEVE was higher than that of BPAGE. While, the photocrosslinking reaction of BPAPE did not take place under the same conditions.

Photoinitiated Michael addition reactions of BPAEVE, BPAPE, and other dipropargyl ethers or ester with pentaerythritol (2-tetramercapto)propionate (PETMP) also proceeded very smoothly to give the gel products by using benzophenone as a photosensitizer in THF. Although the rate of addition reaction of BPAPE was strongly influenced by the photosensitizer concentration, the addition reaction of BPAEVE with PETMP propagated effectively to give the gel products even without the presence of photosensitizer when irradiated with UV light in THF or toluene solution.

INTRODUCTION

Polyfunctional (meth)acrylate monomers and oligomers such as polyurethane (meth)acrylates, polyester (meth)acrylates, polyether (meth)acrylates, and epoxy-(meth)acrylates have been widely used¹⁻⁴ in photocurable or EB-curable coatings, printing inks, solder resists, adhesives, and photoimaging in industry. We have reported on the synthesis of poly[2-(meth)acryloxyethyl vinyl ether]s⁵ by cationic polymerization of vinyloxy ethyl (meth)acrylates and of epoxy-(meth)acrylates by addition reaction of epoxy resins with (meth)acrylic acids⁶ or aryl (meth)acrylates,⁷ and investigated the photocrosslinking reaction of the resulting oligomers so far. It is well known that the photocrosslinking reaction of these (meth)acrylates proceed essen-

tially by the radical polymerization of double bonds in the molecules; however, the polymerization of these monomers and oligomers was strongly inhibited by oxygen in the air.⁸

On the other hand Morgan et al.⁹ proposed a photocrosslinking system based on photoinitiated Michael addition reaction of polyenes with polythiols. Kanehiro and Haniuda have studied¹⁰ the similar photocrosslinking reaction of diallyl compounds having spiro acetal rings with the polythiols. It has been reported^{11,12} recently that the polyaddition reaction of diethynyl compounds with dithiols gave the corresponding soluble polymers in solution or in solid state by the irradiation of UV light. Schlesinger¹³ and Crivello et al.¹⁴ also suggested the crosslinking reactions of polyfunctional epoxy compounds or vinyl ethers, respectively, using cationic photoinitiators such as aryldiazonium, diaryliodonium, or triarylsulfonium salts. These photochemical reaction systems are of interest to the industrial applications of the cured resins because it seems that

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these photocrosslinking systems were not inhibited by oxygen in air.

In this study some photocrosslinking reactions of divinyl ether, dipropargyl ether, dipropargyl esters, and diglycidyl ether were investigated using photosensitizers (or cationic photoinitiators) or without any photosensitizers in solution.

EXPERIMENTAL

Materials

The solvents were purified by distillation prior to use. Michler's ketone (MK) and methoxyhydroquinone (MQ) were recrystallized twice from the suitable solvents. Benzophenone (BP), 2,2-dimethoxy-1,2-diphenylethan-1-one (DMK) (IRGACURE 651; donated by Ciba-Geigy Ltd.), [η^6 -(1-isopropyl)benzene] (η^5 -cyclopentadiene)iron (II) hexafluorophosphate (BCI-PF₆) (IRGACURE 261; donated by Ciba-Geigy Ltd.), 2,5-dibutoxy-4-morpholinobenzene diazonium (MDBZ) salts (donated by Sanbo Chemical Co.), and pentaerythritol (2-tetramercapto)propionate (PETMP) were used without further purification. Diphenyliodonium hexafluorophosphate (DPI-PF₆) and triphenylsulfonium hexafluorophosphate (TPS-PF₆) were prepared according to the reported literature method.¹⁵ Diglycidyl ether of bisphenol-A (BPAGE) (epoxide equivalent: 170.4)¹⁶ was obtained by two successive recrystallization processes of a commercial epoxy resin (DER-332) from the mixed solvent of methanol and ethyl methyl ketone (1 : 4). Di(2-vinyl)oxyethyl ether of bisphenol-A (BPAEVE)¹⁷ and dipropargyl ether of bisphenol-A (BPAPE)^{18,19} were synthesized by the reaction of bisphenol-A with 2-chloroethyl vinyl ether or propargyl bromide, respectively, according to the previously reported methods. 2,2-Hexafluoroisopropylidendi (4-propargyloxybenzene) (BPFPE), 4,4'-dipropargyloxydiphenylsulfone (BPSPE), and dipropargyl terephthalate (DPTP) were also prepared by the reaction of propargyl bromide with the corresponding bisphenols or dicarboxylic acid, respectively, using PTC method.¹⁹

Typical Procedure of Photocrosslinking Reaction Using Cationic Photoinitiator

BPAEVE [0.92 g (2.5 mmol)] and 0.12 g (0.25 mmol) of MDBZ-PF₆ as a cationic catalyst photoinitiator in 25 mL of 1,2-dichloroethane was used. Irradiation of this solution was then performed at 30°C in a small conventional photochemical reactor

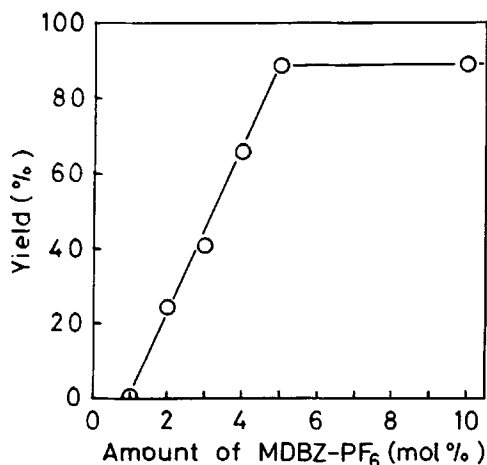


Figure 1 Yield of gel products of the cationic polymerization of BPAEVE using various concentration of MDBZ-PF₆. The reaction was carried out with BPAEVE (10 mmol/dL) in 1,2-dichloroethane (25 mL) at 30°C for 20 min.

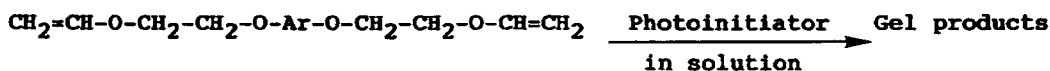
by use of a 500-W high-pressure mercury lamp (Ushio Electric Co., USH-500D) through Pyrex glass filter at a distance of 60 cm (intensity of the irradiation: 30 mW/cm² at 365 nm) under nitrogen atmosphere with magnetic stirring. Nitrogen gas was bubbled through the solution for 20 min before UV irradiation, and then the nitrogen gas stream was passed very slowly through the reaction mixture during exposure. The irradiated solution was poured into 300 mL of methanol. The gel products were filtered using G-4 glass filter, washed with methanol, dried *in vacuo* at 60°C for 24 h, and then the yield was measured.

Typical Procedure of Photocrosslinking Reaction of BPAPE with PETMP

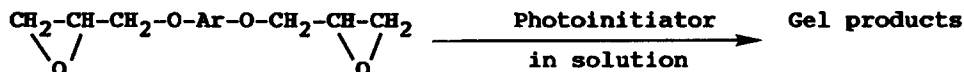
The photochemical reaction of BPAPE [0.61 g (2 mmol)] with PETMP [0.98 g (2 mmol)] was carried out using 0.18 g (0.2 mmol) of BP as a photosensitizer in 25 mL of THF under the same irradiation conditions as applied to the photoinitiated cationic polymerization of BPAEVE.

RESULTS AND DISCUSSION

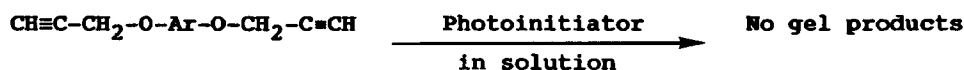
The cationic photocrosslinking reaction of BPAEVE was carried out using various amounts of MDBZ-PF₆ as a cationic photoinitiator in 1,2-dichloroethane at 30°C for 20 min. As shown in Figure 1, the yield of gel products linearly increased with increasing catalyst concentration; however, the yield was saturated at 5 mol % of the catalyst concentration.



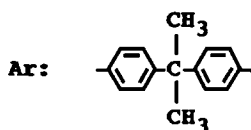
(BPAEVE)



(BPAGE)



(BPAPE)



Scheme I

Correlation between the yield of gel products and the concentration of BPAEVE is shown in Figure 2. Although the gel products was not formed at low monomer concentration, the yield gradually increased with increasing the monomer concentration.

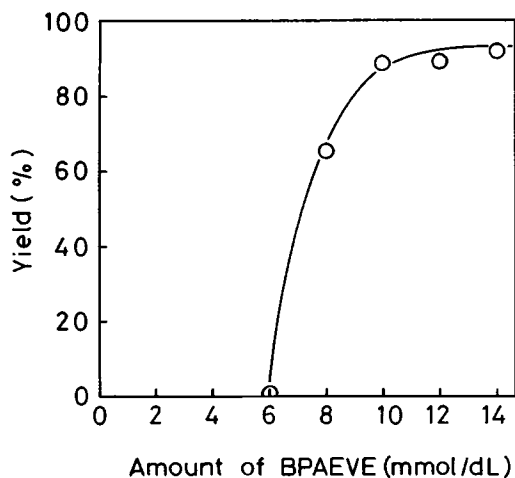


Figure 2 Correlation between the yield of gel products and the BPAEVE concentration on the cationic polymerization. The reaction was carried out using MDBZ-PF₆ (5 mol %) in 1,2-dichloroethane (20 mL) for 20 min at 30°C.

These results indicate that the rate of photocrosslinking reaction of BPAEVE with cationic photoinitiator in 1,2-dichloroethane solution was strongly affected by the monomer concentration and the catalyst concentration.

The cationic photocrosslinking reactions of BPAEVE, BPAPE, and BPAGE were performed under the fixed monomer and catalyst concentration using MDBZ-PF₆ in 1,2-dichloroethane at 30°C (Fig. 3). The result clearly shows that the rate of gel production of BPAEVE was higher than that of BPAGE. Similar results of the cationic polymerizations of these monomers have also been found from DSC analysis by Crivello et al.¹⁴

The catalytic effect of various cationic photoinitiators on the reaction of BPAEVE and BPAPE is summarized in Table I. This result indicates that the rate of gel production of BPAEVE was strongly influenced by the acidity of Lewis acid, and the rate of gel production of BPAEVE in 1,2-dichloroethane increased in the order BF₄⁻ < PF₆⁻ < SbF₆⁻, although Crivello et al. have reported¹⁴ that the rate of photoinitiated cationic polymerization of BPAEVE did not affect by the kind of counterion when diphenyliodonium salts were used as the cationic photoinitiators.

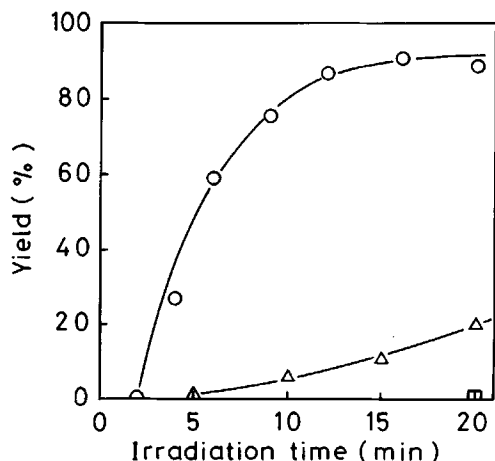


Figure 3 The rate of gel production of the cationic polymerization of BPAEVE, BPAPE, and BPAGE. The reaction was carried out with monomer (10 mmol/dL) using MDBZ-PF₆ (5 mol %) in 1,2-dichloroethane (25 mL) at 30°C. (○) BPAEVE, (□) BPAPE, (△) BPAGE.

Furthermore, it was found that DPI-PF₆ (λ_{\max} = 302 nm, ϵ_{\max} = 1743 in anisole), TPS-PF₆ (λ_{\max} = 298 nm, ϵ_{\max} = 447 in anisole), and BCI-PF₆ (λ_{\max} = 300 nm, ϵ_{\max} = 1373 in anisole) with weak absorption at 300–400 nm had excellent catalytic activity as did MDBZ-PF₆, which has strong absorption at 300–400 nm (λ_{\max} = 401 nm, ϵ_{\max} = 27500 in anisole), for the cationic photocrosslinking reaction of BPAEVE in 1,2-dichloroethane. This result means that effective cationic polymerization of divinyl ether moieties in BPAEVE proceeded due to

Table I Yield of Gel Products on the Photochemical Reaction of BPAEVE and BPAPE using Various Cationic Photoinitiators^a

Monomer (mmol/dL)	Cationic Photoinitiator (mol %)	Yield of Gel Products (wt %)
BPAEVE (10)	MDBZ-SbF ₆ (4)	100
BPAEVE (10)	MDBZ-PF ₆ (4)	66
BPAEVE (10)	MDBZ-PF ₆ (5)	88
BPAEVE (10)	MDBZ-BF ₄ (4)	59
BPAEVE (10)	DPI-PF ₆ (5)	95
BPAEVE (10)	TPS-PF ₆ (5)	97
BPAEVE (10)	BCI-PF ₆ (5)	96
BPAPE (20)	MDBZ-PF ₆ (10)	0
BPAGE (10)	DPI-PF ₆ (5)	3
BPAGE (10)	TPS-PF ₆ (5)	12

^a The reaction was carried out in 1,2-dichloroethane (25 mL) for 20 min (37.8 J/cm²; measured at 365 nm) at 30°C.

the small amounts of photoinitiated cationic species derived from DPI-PF₆, TPS-PF₆, or BCI-PF₆, and BPAEVE produced very smooth gel products with 20 min irradiation.

On the other hand the yield of gel products was very small in the cationic photocrosslinking reaction of BPAPE using MDBZ-PF₆, DPI-PF₆, or TPS-PF₆ under the same irradiation conditions. This result indicates that the rate of gel production of polyfunctional monomers was strongly affected by the kind of functional group in the molecule in the 1,2-dichloromethane solution, although the rate of gel production was also affected by the photochemical reactivity of the catalysts as well as by the monomer concentration and the catalyst concentration.

Interestingly enough, the cationic photocrosslinking reaction of BPAPE did not occur in 1,2-dichloroethane solution (Fig. 3 and Table I), although polymer film containing pendant propargyl esters in the presence of MDBZ-PF₆ showed²⁰ very high practical photosensitivity as negative-type photoresist. It seems that photoinitiated cationic reactions of propargyl moieties were strongly affected by the concentration of functional groups.

As summarized in Table II, BPAEVE, BPAPE, and other dipropargyl compounds with 10 mol % of BP as a photoinitiator did not form any gel products by the irradiation of UV light in THF solution at 30°C for 20 min. On the other hand gel products were obtained in high yield when the photochemical reactions were carried out in the presence of equivalent amounts of polyfunctional thiol PETMP. This

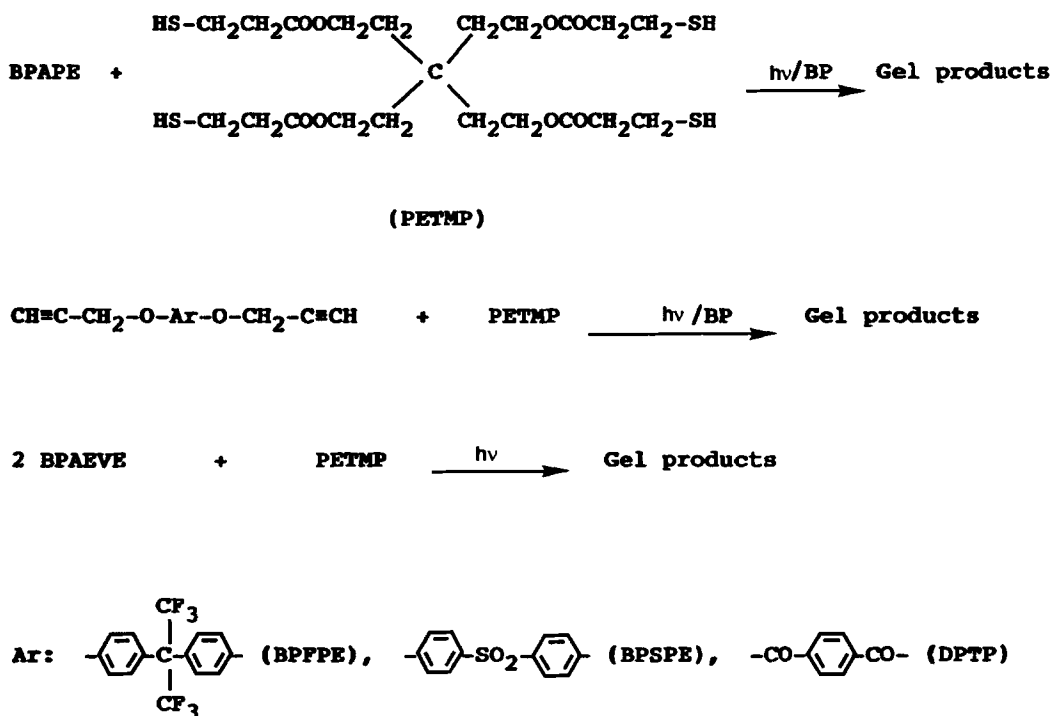
Table II Yield of Gel Products on the Photochemical Michael Addition Reaction of Divinyl or Dipropargyl Compounds with PETMP^a

Monomer I	Monomer II	Yield of Gel Products (wt %)
BPAEVE	—	0
BPAPE	—	0
BPFPE	—	0
BPSPE	—	0
DPTP	—	0
BPAPE	PETMP	97
BPFPE	PETMP	89
BPSPE	PETMP	85
DPTP	PETMP	93

^a The reaction was carried out with monomer I (2 mmol) and monomer II (2 mmol) using 10 mol % of BP in THF (25 mL) at 30°C for 20 min.

means that photoinitiated Michael addition reaction between divinyl or dipropargyl compounds with thiol groups in PETMP proceeded very smoothly using

BP as the photosensitizer in THF solution, although photoinitiated radical homopolymerization of divinyl or dipropargyl compounds did not occur under the same conditions.



Scheme II

As shown in Figure 4, the yields of gel products increased with increasing monomer concentration when the photochemical reaction of BPAEVE (supposed as difunctional monomer) and BPAPE (supposed as tetrafunctional monomer) with equivalent amounts of PETMP (supposed as tetrafunctional monomer) was carried out using 10 mol % of BP (to PETMP) as the sensitizer in THF at 30°C for 20 min. This result indicates that both photochemical Michael addition reactions of BPAEVE and BPAPE with PETMP were strongly affected by the monomer concentration, and the photochemical reactivity of BPAPE was slightly lower than that of BPAEVE under the same irradiation conditions.

The photochemical reaction of equivalent amounts of BPAPE with PETMP was carried out without BP, or with 1 or 10 mol % of BP, respectively. As shown in Figure 5, the photocrosslinking reaction hardly occurred without BP; however, the yield of gel products increased dramatically using BP as the photosensitizer. This means that the photochemical reaction started mainly from the excitation of BP.

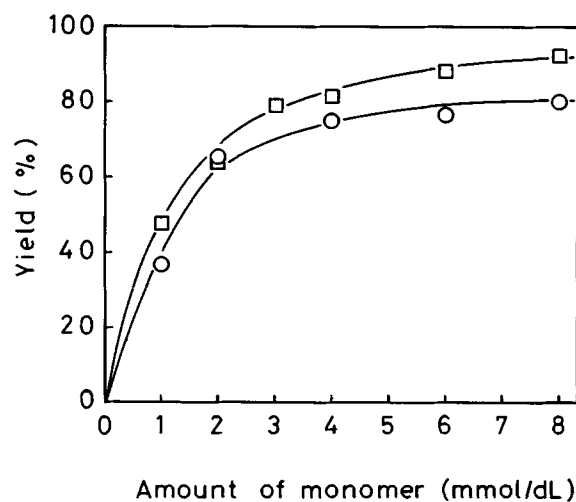


Figure 4 Correlation between the yield of gel products and the monomer concentration on the Michael addition reaction of BPAEVE and BPAPE with PETMP. The reaction was carried out using BP (10 mol % to PETMP) in THF (25 mL) at 30°C for 20 min. (□) BPAEVE, (○) BPAPE.

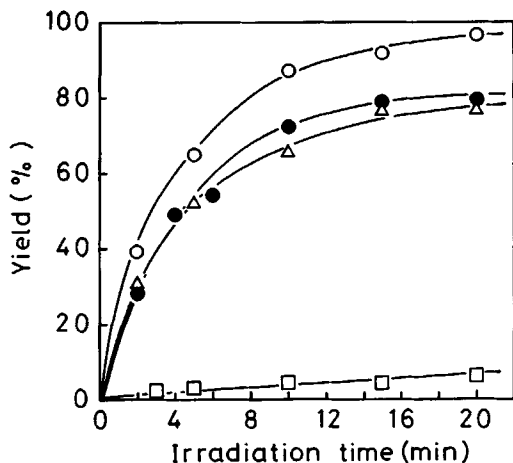


Figure 5 The rate of gel production on the Michael addition reaction of BPAGE with PETMP. The reaction was carried out with BPAGE (8 mmol/dL) and PETMP (8 mmol/dL) in THF (25 mL) at 30°C. (O) with 10 mol % of BP, (Δ) with 1 mol % of BP, (□) without BP, (●) with half amounts of PETMP (4 mmol/dL), and 10 mol % of BP.

BPAGE can also be presumed to be a difunctional monomer; therefore, the photochemical reaction of BPAGE with half amounts of PETMP was carried out using 10 mol % of BP in THF solution (Fig. 5). However, the rate of gel production was lower than that of the reaction with an equivalent amount of PETMP. We have found²¹ recently that pendant propargyl ester groups in the polymer reacted with about 1.5 times amounts of thiophenol using BP as the photosensitizer in solution. Therefore, it seems reasonable to consider that BPAGE is a tetrafunctional monomer for the photoinitiated Michael addition reaction with thiol compounds.

As shown in Figure 6, the rate of photochemical reaction of BPAGE with PETMP was dependent on the kind of photosensitizer; that is, BP and DMK had higher photosensitization efficiencies than MK on the reaction.

On the other hand the photoinitiated Michael addition reaction of BPAEVE with PETMP proceeded very smoothly without any photosensitizers by the irradiation of UV light, although the reaction was enhanced by the addition of BP (Fig. 7). This is very interesting and useful result for applications to the coating technology, although detailed reaction mechanism is not very clear yet. It seems that BPAEVE was directly excited by irradiation with UV light, followed by reaction of excited divinyl monomer with the thiol compound.

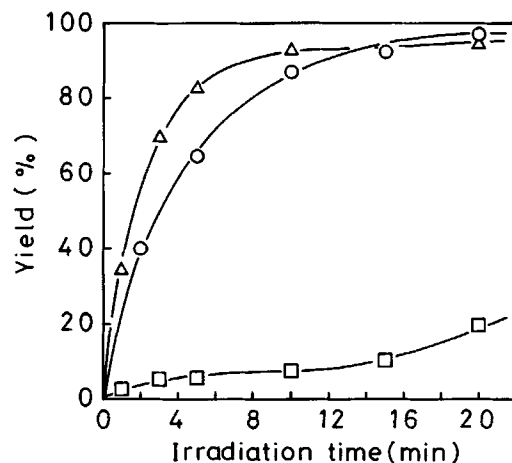


Figure 6 The rate of gel production on the reaction of BPAGE with PETMP using various photosensitizers. The reaction was carried out with BPAGE (8 mmol/dL) and PETMP (8 mmol/dL) using the photosensitizer (10 mol %) in THF (25 mL) at 30°C. (O) BP, (Δ) DMK, (□) MK.

The reactions of BPAGE and BPAEVE with PETMP were carried out in the presence of various amounts of BP in THF at 30°C for 10 min, and detail correlations between yields of gel products and BP concentration are summarized in Figure 8. The result suggests that the yield of gel products of BPAEVE was hardly affected by the BP concentration, whereas the yield of gel products of BPAGE was strongly dependent on the BP concentration.

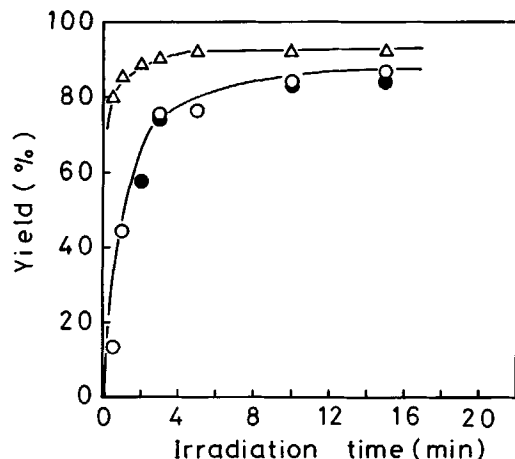


Figure 7 The rate of gel production on the reaction of BPAEVE with PETMP. The reaction was carried out with BPAEVE (8 mmol/dL) and PETMP (4 mmol/dL) in the solvent (25 mL) at 30°C. (Δ) with 1 mol % of BP in THF, (O) without BP in THF, (●) without BP in toluene.

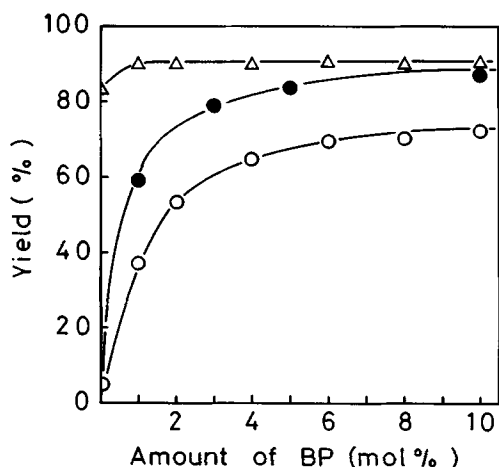


Figure 8 Correlation between the yield of gel products and the BP concentration on the reaction of BPAEVE and BPAPE with PETMP. The reaction was carried out with BPAEVE (8 mmol/dL) or BPAPE (8 mmol/dL) and PETMP (4 mmol/dL) in THF (25 mL) at 30°C for 10 min. (Δ) BPAEVE, (○) BPAPE, (●) BPAPE with two times amounts of PETMP (8 mmol/dL).

Furthermore, photocrosslinking reaction of BPAEVE with PETMP without any photosensitizer was carried out in the presence of various amounts of MQ, which is well known as a typical radical inhibitor, in THF solution at 30°C (Fig. 9). Interestingly enough, the reaction proceeded smoothly to give the gel products 10 mol % even when MQ was added, although the rate of photochemical reaction

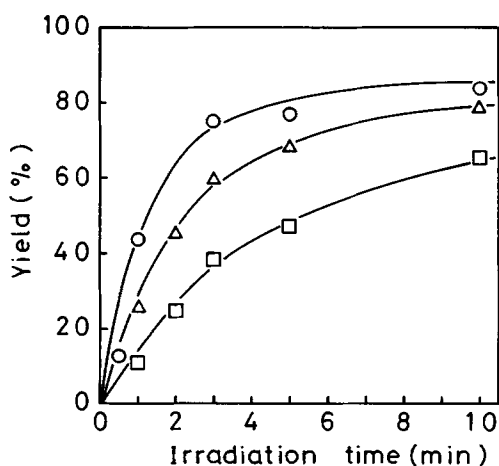


Figure 9 The rate of gel production on the no sensitized photochemical reaction of BPAEVE with PETMP. The reaction was carried out with BPAEVE (8 mmol/dL) and PETMP (4 mmol/dL) in the presence of MQ in THF (25 mL) at 30°C. (○) without MQ, (Δ) with 1 mol % of MQ, (□) with 10 mol % of MQ.

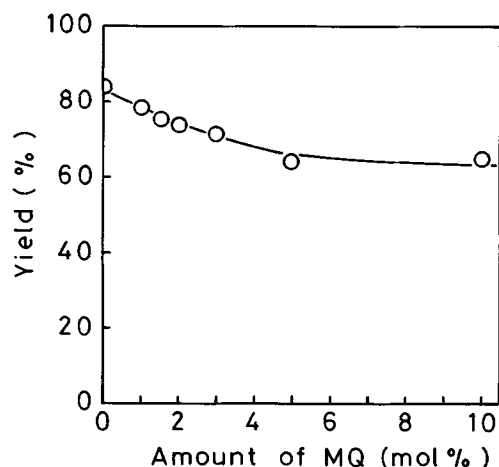


Figure 10 Correlation of the yield of gel products and the MQ concentration on the no photosensitized reaction of BPAEVE with PETMP. The reaction was carried out with BPAEVE (8 mmol/dL) and PETMP (4 mmol/dL) in THF (25 mL) at 30°C for 10 min.

was depressed by the addition of MQ. Detail correlation between the yield of gel products and the MQ concentration is shown in Figure 10. This suggests that the yield of gel products decreased gradually with increasing the MQ concentration. However, the reaction of BPAEVE with PETMP produced the gel products with relatively high yield even in the presence of large amounts of radical inhibitor MQ, because it might be considered that thiol group in PETMP had higher radical reactivity than the phenol group in MQ.

From all these results the following conclusions can be obtained: (1) The rate of gel production of BPAEVE by using cationic photoinitiator was much higher than that of BPAPE. (2) The photocrosslinking reaction of BPAPE with cationic photoinitiator did not take place under the same conditions. (3) The photoinitiated Michael addition reactions of BPAPE and other dipropargyl monomers with PETMP occurred effectively using BP as a photosensitizer. (4) The photochemical addition reaction of BPAEVE with PETMP proceeded very smoothly even without any photosensitizer, although the reaction was enhanced by the addition of BP. (5) BPAEVE is a conventional polyfunctional monomer for the photoinitiated cationic polymerization as well as the photoinitiated Michael addition reaction with polythiols. (6) BPAPE and other dipropargyl compounds are also useful new polyfunctional monomers for the photoinitiated Michael addition reaction with polythiols.

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