

Notes

Photopolymerization of Methyl Methacrylate Initiated by Benzoin Derivatives

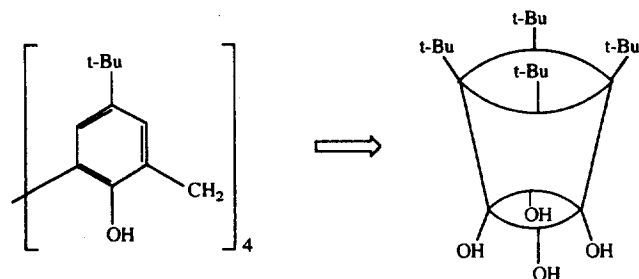
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Photopolymerization of vinyl monomers has received an extensive attention. The most obvious merits might be the notable convenience of being able to simply, cleanly, and rapidly perform a reaction. Photopolymerization technology is commercially used today in the areas of surface coatings, photoresists, adhesives, and holography.¹ Although any vinyl monomer that will undergo chain reaction polymerization is subject to photopolymerization or photosensitized polymerization, only a few unsaturated monomers are known to absorb light between 250 and 500 nm which is the most convenient wavelength range for experimental work. The detailed mechanism of the formation of the propagating radicals in the initiator-free photopolymerization is not completely understood, but it appears to involve the conversion of an electronically excited singlet state of the monomer to a long-lived excited triplet state.² However, even if such direct light absorption by a monomer does occur, the polymerization of monomer can be accelerated if a photoinitiator is present.

Silicon compounds have been widely used in polymerization reactions by dehydrogenative Si-Si coupling^{3a}, hydrosilyation^{3b}, and group transfer^{3c}. There are few reports on the silicon compound-initiated photopolymerization of unsaturated monomers.⁴ Cyclic, bowl or basket-shaped calixarene molecules, produced by condensation of *p*-substituted phenols with formaldehyde, are well known to exhibit a host-guest inclusion chemistry.⁵



Calixarenes might activate or deactivate the photopolymerization via a host-guest interaction with the photogenerated radical species. Intensive studies on the photopolymerization of vinyl monomers initiated by benzoin-derived photoinitiators including benzoin ethers have been made.^{6,10-12} Recently, Gruber and coworkers prepared the silicon-containing photoinitiators such as 1-(4-dimethylsilyl)phenyl-2-hydroxy-2-methyl-propan-1-one and 1-(4-dimethylsilyl)phenyl-2-

methoxy-2-methyl-propan-1-one, and examined their photoinitiating efficiency.⁷ However, the photopolymerization initiated by benzoin silyl ethers has not been reported to date. The silyl group of the benzoin silyl ether could have the electron-releasing and sterically bulky natures. The electron-donating ability of the silyl group could help the α -photocleavage of the benzoin silyl ethers, but its steric bulkiness could deter the attack of the resulting radicals on vinyl monomers. In the present paper we report the preparation of benzoin silyl ethers and the photopolymerization of methyl methacrylate initiated by various benzoin derivatives under the influence of solvent and calixarene.

Experimental Section

Materials and Instrumental. All reactions and manipulations were performed under prepurified nitrogen using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. Elemental analyses were performed by Galbraith Laboratories, Inc.. Infrared spectra were obtained using a Nicolet 520P FT-IR spectrometer. Electronic spectra were acquired using an IBM 9420 UV-VIS spectrophotometer. Proton NMR spectra were recorded on a Bruker ASX 32 (300 MHz) spectrometer using $\text{CDCl}_3/\text{CHCl}_3$ as a reference at 7.24 ppm downfield from TMS. For the photolysis experiments a Raynot photochemical reactor model RPR-208 made by The Southern N.E. Ultraviolet Co., which has merry-go-round system in order to uniformly irradiate all samples, was used. The built-in monochromatic UV light sources (RUL-300 nm UV lamp; lamp intensity = $6.93 \times 10^{18} \text{ hv} \cdot \text{mL}^{-1} \cdot \text{min}^{-1}$)⁸ was positioned approximately 17 cm from the reaction quartz tube. The heat generated by the lamp caused the internal temperature to increase to 36 °C. Gel permeation chromatography (GPC) was carried out on a Waters Millipore GPC Liquid Chromatograph. The calibrant (monodisperse polystyrene) and the sample were dissolved in THF and separately eluted from an Ultrastayragel GPC column series (sequence 10³, 10⁴, 10⁵, 10⁶ Å columns). Molecular weights were extrapolated from the calibration curve derived from the polystyrene standard. Data analyses were carried out using a Waters Data Module 570. Benzophenone and benzoin (Aldrich Chemical Co.) were recrystallized from ethanol before use. Benzoin ethyl ether and benzoin isobutyl ether (Aldrich Chemical Co.) were used without further purification. Methyl methacrylate (Jensei Chemical Co.) was washed twice with aqueous 5% NaOH (to remove inhibitor), washed twice with distilled water, dried over MgSO_4 , and distilled at reduced pressure before use. Me_3SiCl , PhSiCl_3 , Ph_2SiCl_2 , and PhMeSiCl_2 (Hüls America, Inc.) were distilled before use. Benzoin benzoate and benzoin acetate were prepared according to the literature procedure.⁹ *p*-*tert*-Butylcalix[4]arene was kindly provided by professor Kye-Chun Nam at Chonnam National University.

Preparation of Benzoin Trimethylsilyl Ether (BTSE). The following procedure is representative of the preparation of benzoin silyl ethers. To a stirred solution of

benzoin (4.25 g, 20 mmol) in a mixed solvent of diethyl ether (25 mL) and pyridine (5 mL) was added a solution of Me_3SiCl (2.54 mL, 20 mmol) in diethyl ether (10 mL). After 2 h, 50 mL of benzene was added to the reaction mixture. The mixture was filtered and the filtrate was concentrated under reduced pressure to saturation. Hexane (50 mL) was added. The precipitate was filtered off, washed with hexane, and dried *in vacuo*. Benzoin trimethylsilyl ether was obtained in 60% yield (3.40 g) as an off-white powder. Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{Si}$: C, 71.79; H, 7.09. Found: C, 70.47; H, 6.97. IR (KBr pellet, cm^{-1}): 1670 s ($\nu\text{C}=\text{O}$), 1070 s ($\nu\text{Si}-\text{O}$). ^1H NMR (δ , CDCl_3 , 300 MHz): 0.07 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 5.97 (s, 1H, CH), 7.2-8.7 (m, 10H, ArH).

Preparation of Bis(benzoin)phenylmethylsilyl Ether (BPSE). 40% yield. Off-white powder. Anal. Calcd for $\text{C}_{35}\text{H}_{30}\text{O}_4\text{Si}$: C, 77.46; H, 5.57. Found: C, 76.73; H, 5.21. IR (KBr pellet, cm^{-1}): 1698 s ($\nu\text{C}=\text{O}$), 1070 s ($\nu\text{Si}-\text{O}$). ^1H NMR (δ , CDCl_3 , 300 MHz): 0.35 (s, 3H, $\text{Si}-\text{CH}_3$), 5.95 (s, 2H, CH), 7.2-8.6 (m, 25H, ArH).

Preparation of Bis(benzoin)diphenylsilyl Ether (BDSE). 40% yield. Off-white powder. Anal. Calcd for $\text{C}_{40}\text{H}_{32}\text{O}_4\text{Si}$: C, 79.44; H, 5.33. Found: C, 78.68; H, 5.01. IR (KBr pellet, cm^{-1}): 1670 s ($\nu\text{C}=\text{O}$), 1060 s ($\nu\text{Si}-\text{O}$). ^1H NMR (δ , CDCl_3 , 300 MHz): 5.96 (s, 2H, CH), 7.0-8.0 (m, 30H, ArH).

Preparation of Tris(benzoin)phenylsilyl Ether (TPSE). 45% yield. Off-white powder. Anal. Calcd for $\text{C}_{48}\text{H}_{38}\text{O}_6\text{Si}$: C, 78.02; H, 5.18. Found: C, 76.53; H, 4.99. IR (KBr pellet, cm^{-1}): 1673 s ($\nu\text{C}=\text{O}$), 1060 s ($\nu\text{Si}-\text{O}$). ^1H NMR (δ , CDCl_3 , 300 MHz): 5.96 (s, 3H, CH), 7.2-8.0 (m, 35H, ArH).

Photopolymerization of Methyl Methacrylate (MMA) by Benzoin Derivatives. The following procedure is representative of photopolymerization reactions. A quartz test tube (1 cm \times 20 cm) charged with MMA (2.14 mL, 20 mmol), BTSE (3.7 mg, 13 μmol), and benzene (13 mL) was degassed, sealed, and irradiated with UV-light for 2 h (equivalent to 8.3×10^{20} $\text{hv} \cdot \text{mL}^{-1}$). The polymer was precipitated in hexane, filtered off, and dried to give 0.22 g (11%) of poly(MMA).

Photopolymerization of MMA with Benzoin-Derived Photoinitiator in the Presence of *p*-tert-Butylcalix[4]arene. The following procedure is a typical example of the photopolymerization reactions. A quartz test tube (1 cm \times 20 cm) was loaded with MMA (2.14 mL, 20 mmol), BTSE (3.7 mg, 13 μmol), *p*-tert-butylcalix[4]arene (1.4 mg, 2.0 μmol) and benzene (13 mL). The mixture was degassed, sealed, and irradiated with UV-light for 2 h (equivalent to 8.3×10^{20} $\text{hv} \cdot \text{mL}^{-1}$). The polymer was precipitated in hexane, filtered off, and dried to give 0.21 g (11%) of poly(MMA).

Thermal Polymerization of MMA with Benzoin-Derived Photoinitiator in the Presence of *p*-tert-Butylcalix[4]arene. The following procedure is a typical example of thermal polymerization reactions. A test tube (1 cm \times 20 cm) was charged with MMA (2.14 mL, 20 mmol), BTSE (3.7 mg, 13 μmol), *p*-tert-butylcalix[4]arene (1.4 mg, 2.0 μmol) and benzene (13 mL). The mixture was degassed, sealed, and heated at 75 $^\circ\text{C}$ for 24 h. The polymer was precipitated in hexane, filtered off, and dried to give just small amount of poly(MMA).

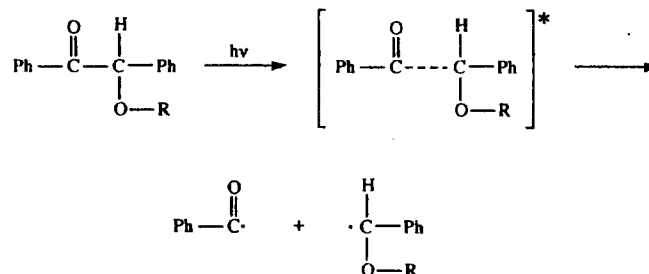
Photopolymerization of MMA with BDSE in Different Solvent. The following procedure is representative of photopolymerization reactions. A quartz test tube (1 cm \times

20 cm) loaded with MMA (2.14 mL, 20 mmol), BDSE (7.9 mg, 13 μmol), and THF (13 mL) was degassed, sealed, and irradiated with UV-light for 2 h (equivalent to 8.3×10^{20} $\text{hv} \cdot \text{mL}^{-1}$). The polymer was precipitated in hexane, filtered off, and dried to give 0.555 g (28%) of poly(MMA). The same polymerization was also carried out in benzene and methanol, respectively.

Results and Discussion

The benzoin silyl ethers such as benzoin trimethylsilyl ether (BTSE), bis(benzoin)phenylmethylsilyl ether (BPSE), bis(benzoin)diphenylsilyl ether (BDSE), and tris(benzoin)phenylsilyl ether (TPSE) were prepared by reacting benzoin with corresponding chlorosilane in the presence of pyridine. The chemical shifts associated with the proton of the C-H bond in the ^1H NMR spectra of the benzoin silyl ethers are in the ranges of 5.9-6.0 ppm. The C=O and Si-O stretching bands in the IR spectra of the silyl ethers are in the 1670-1700 cm^{-1} and 1060-1070 cm^{-1} range, respectively. The molar extinction coefficients of the benzoin silyl ethers in THF were found to be *ca.* 780 $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ and were similar to the those of benzoin esters (*i.e.*, 770 $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for BA and 773 $\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ for BB).⁸

Benzoin alkyl ethers are known to undergo α -photocleavage to benzoyl radical and alkoxybenzyl radical as follows:¹⁰



The inability to quench photocleavage of benzoin alkyl ethers with triplet quenching agents suggested that reaction may occur via dissociation of the excited singlet states. It is known that electron-donating groups on the benzyl group and electron-attracting groups on the benzoyl group facilitates α -photocleavage, which is attributed to polar contribution in the activated complex being excited singlet state.¹⁰ In the absence of unsaturated monomers, benzoyl radical can dimerize to benzil or can abstract hydrogen from a hydrogen-donor molecule and produce benzaldehyde and alkyl radical. Alkoxybenzyl radicals can dimerize to pinacol ether or be cleaved to benzaldehyde and alkyl radical. In the presence of unsaturated monomers, the radicals can initiate the polymerization of the monomers. Overeen and coworkers reported that these two radicals are not equally effective and the benzoyl radical mainly involves in the chain propagation of the photopolymerization.¹¹ However, the interpretation has been challenged by Asmus *et al.* on the basis of studies utilizing α -methoxy benzyl radical independently photogenerated by H-abstraction from benzyl methyl ether as photoinitiator for MMA polymerization.¹² They claimed that the benzyl radical can equally participate in the chain propagation of the photopolymerization.

One of us reported a detailed study on the photopolymeri-

Table 1. Photopolymerization of MMA Initiated by Benzoin Derivatives^a

Initiator	Percent conversion	
	Absence of <i>p</i> - <i>tert</i> -butylcalix[4]arene	Presence of <i>p</i> - <i>tert</i> -butylcalix[4]arene
BEE	29	31
BIE	26	26
BA	11	10
BTSE	11	11
BPSE ^b	10	10
TPSE ^c	10	10
BZH	10	14
BB	5	7

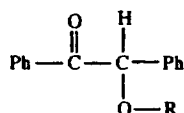
^aMMA, 20 mmol; initiator, 1.3×10^{-2} mmol; *p*-*tert*-butylcalix[4]arene, 2.0×10^{-3} mmol in benzene (13 mL); UV-irradiation for 2 h. ^bBPSE, 6.5×10^{-3} mmol. ^cTPSE, 4.3×10^{-3} mmol.

Table 2. GPC Characterization of Photopolymerization of MMA^a

Initiator	mol wt ^b	
	M_w	M_n
BEE	51000	34000
BIE	26000	13000
BA	232000	99000
BTSE	260000	30000
BPSE ^c	161000	67000
TPSE ^d	167000	48000
BZH	165000	46000
BB	249000	66000

^aMMA, 20 mmol; initiator, 1.3×10^{-2} mmol; *p*-*tert*-butylcalix[4]arene, 2.0×10^{-3} mmol in benzene (13 mL); UV-irradiation for 2 h. ^bMeasured with GPC in THF. ^cBPSE, 6.5×10^{-3} mmol. ^dTPSE, 4.3×10^{-3} mmol.

zation of acrylic acid derivatives using benzoin alkyl ethers.^{6d} We have carried out the photopolymerization of methyl methacrylate (MMA) with benzoin derivatives such as benzoin (BZH), benzoin silyl ethers (BTSE, BPSE, BDSE, TPSE), benzoin alkyl ethers (benzoin ethyl ether (BEE) and benzoin isobutyl ether (BIE)), and benzoin esters (benzoin acetate (BA) and benzoin benzoate (BB)) in benzoin in the presence and absence of *p*-*tert*-butylcalix[4]arene (Table 1 and 2).



R = H, BZH; Et, BEE; ^tBu, BIE;
C(=O)Me, BA; C(=O)Ph, BB;
SiMe₃, BTSE; SiPhMe(BZ), BPSE;
SiPh₂(BZ), BDSE; SiPh(BZ)₂, TPSE

The percent conversion of MMA to poly(MMA) decreased within the experimental error range in the order BEE > BIE > BTSE ≈ BPSE ≈ TPSE ≈ BZH ≈ BA > BB. Benzoin ethyl ether (BEE) and benzophenone (BP) were found to give the best and worst polymer formation, respectively, and the polymer formation in the photopolymerization exhibited a general order benzoin alkyl ether > benzoin silyl ether ≥ benzoin ester.

Table 3. Solvent Effect on the Photopolymerization of MMA Initiated by BDSE^a

Solvent	Percent conversion	mol wt ^b	
		M_w	M_n
benzene	17	35000	13000
methanol	21	165000	48000
THF	28	42000	14000

^aMMA, 20 mmol; BDSE, 1.3×10^{-2} mmol in solvent (13 mL); UV-irradiation for 2 h. ^bMeasured with GPC in THF.

While the weight average molecular weight generally increases with increase of conversion in the radical polymerization, the molecular weights of the polymers did not correspond to the polymer formation as shown in Table 1 and 2. We cannot rationalize this at the present moment. The order of percent conversion BEE > BIE is due probably to different steric effect imposed by the alkoxy groups. Alkyl radicals are generally pyramidal (sp³ hybrid), and most radicals are between pyramidal and planar. Radical geometry is significantly affected by substituent group: π-donor group and smaller group favor a pyramidal structure.¹³ The benzyl radical with ethoxy group from BEE should favor a pyramidal geometry more than that with isopropoxy group from BIE. Thus, the benzyl radical with ethoxy group can attack on vinyl group of MMA monomer molecule better than that with isopropoxy group. Benzoin silyl ethers were found to afford less polymer formation than benzoin alkyl ethers. The size of the siloxy groups *per se* is much larger than that of the alkoxy groups, and the steric effect is furthermore amplified by the angle between Si-O-C bonds wider than the angle between C-O-C bonds due to *p*-*n*-*d**n* overlap between vacant *d*-orbital of Si and filled *p*-orbital of C.¹⁴ The percent conversions of MMA to poly(MMA) by silyl ethers are similar in the experimental error range although the molecular weights are different. Interestingly, the effect of benzoin esters on the polymer formation is similar to benzoin silyl ethers. The reason is probably because the steric and electronic effect imposed by the siloxy groups can be comparable to the steric and electronic effect exerted by the ester groups. The reason that BA gives the higher polymer formation than BB could be due to steric effect: the acetate group is smaller than the benzoate group. We know from the facts discussed above that both benzoyl and benzyl radicals seemed to equally involve in the chain propagation of the photopolymerization. Very interestingly, as shown in Table 1, *p*-*tert*-butylcalix[4]arene, which is a potent inhibitor for radical polymerization and is expected to show an activation effect of radicals by host-guest interaction, apparently did not affect the photopolymerization of MMA. The reason is probably because the (*n*, π*) transition of the aromatic alcohol groups of the calixarene by 300 nm UV light⁵ and a host-guest interaction between the radicals and calixarene are hardly made. Aliphatic alcohols have their longest absorption band at wavelength below 200 nm associated with an (*n*, π*) transition. Photolysis of aliphatic alcohols in the condensed phase is negligible at the wavelength.¹⁵ The IR stretching bands of OH groups of calix[4]arenes appear at *ca.* 3150 cm⁻¹. The unusually low frequency is attributed to the very strong intramolecular

hydrogen bonding, "circular hydrogen bonding".^{16a} Thus, calix[4]arenes have very low pK_a value and acidic character,^{16b} and used as stabilizers for various organic polymers.¹⁷ Solvents affected on the photopolymerization of MMA (Table 3).

Polymer formation decreased in the order THF>methanol>benzene. Solvent polarity does not account for the tendency of the polymer formation because the solvent polarity follows the order methanol>THF>benzene. The order of the solvent polarity corresponds to the order of polymer molecular weights. While the radical polymerization in methanol does not generally produce the high molecular weight of polymer, the high molecular weight of the polymer in our study was obtained as shown in Table 3. We do not have the rationalization for this at the present moment.

In conclusion, the percent conversion of the photopolymerization of MMA were found to depend upon structure of photoinitiators and solvents, but apparently not to be affected by calixarene.

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A Practical and Large Scale Synthesis of Phenyl Vinyl Sulfone from Benzenethiol and 2-Chloroethanol

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Vinyl sulfones, and in particular phenyl vinyl sulfone, have now become generally accepted as useful intermediates in organic synthesis.¹ The synthetic utility²⁻³ of phenyl vinyl sulfone derives from their ability to serve not only as excellent Michael acceptors toward such reagents as enolate anions and organometallics but also as moderately reactive dienophiles in Diels-Alder reactions.

In connection with our research project, we required a large quantity of phenyl vinyl sulfone as an intermediate. Although phenyl vinyl sulfone is commercially available, it is very expensive. Literature⁴ survey shows that applicable strategy for the preparation of phenyl vinyl sulfone involves the dehydrohalogenation of β -haloethyl phenyl sulfone which can be obtained by oxidation of the corresponding sulfide. Whereas β -haloethyl phenyl sulfide can be prepared by alkylation of benzenethiol with 1,2-dihaloethane, this reaction gives 1,2-bis(phenylthio)ethane as a byproduct.⁵ The purpose of this paper is to describe a practical, versatile, high-yield synthesis of phenyl vinyl sulfone.

The preparation of phenyl vinyl sulfone began with the condensation of benzenethiol **1** with 2-chloroethanol **2** in the presence of sodium hydroxide. The alkylation of benzenethiol **1** with 2-chloroethanol **2** or 2-bromoethanol gave phenyl 2-hydroxyethyl sulfide **3** quantitatively with high purity. The previous published method for obtaining phenyl 2-haloethyl sulfide from 1,2-dihaloethane proceeded in low yield and afforded 1,2-bis(phenylthio)ethane as a side product. This pro-