

Photopolymerization of Vinyl Monomers Using Organic Initiators

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Abstract

This miniaccount presents the selective examples of our recent discoveries in the photopolymerization of vinyl monomers using the organic initiators such as hydrosilanes, poly(hydroarylsilane)s, benzoin silyl ethers, and thianthrene cation radical. In the photopolymerization of vinyl monomers with silanes polysilanes, while the polymerization yields and polymer molecular weights of the poly(MMA)s containing the silyl moieties decreased, the TGA residue yields and intensities of SiH stretching IR bands increased as the mole ratio of the silanes over MMA increased. The hydroarylsilane and poly(hydroarylsilane) seemed to influence strongly on the photopolymerization of olefinic monomers as both chain initiation and chain transfer agents. For the photohomopolymerization and photocopolymerization of MA and AA, the similar trends were observed. Benzoin silyl ethers and thianthrene cation radical also exhibit the photoinitiating ability in the photopolymerization of MMA.

Key words : Photopolymerization, Radical chain polymerization, Vinyl monomers, Hydrosilane, Hydrosilation, Chain initiation, Chain transfer, Poly(hydrosilane), Copolymerization, Graft polymerization, Hydrosilapolymerization, Benzoin silyl ether, Thianthrene cation radical.

1. Introduction

The term *photoinitiation* or *photoinduction* means the process initiated by electromagnetic radiation which is a form of energy. The energy of electromagnetic radiation decreases in the order: γ -rays > X-rays > ultraviolet (UV) > visible (Vis) > infrared (IR) > microwaves > radio waves. UV and IR lights are also divided into subgroups: e.g., extreme UV, far UV, near UV.^[1] *Photoinitiated polymerization* (or *photoinduced polymerization* or *photopolymerization*) occurs when active species (e.g., radical, cationic and anionic) are produced by light irradiation of a reaction system. Generally, the photopolymerization occurs when radicals are produced by UV or visible light irradiation of a reaction system.^[2] The term *photosensitized polymerization* is used when the polymerization occurs by an energy transfer mechanism as a second pathway. Chain radical photopolymerization of vinyl monomers has received a considerable amount of attention due to its practical merits. The most obvious

advantages might be the marked convenience and the avoidance of chemical contamination by initiator residues. Photopolymerization technology is globally used on a commercial scale today in the areas of surface coatings, printing inks, photoresists, adhesives, and holography.^[3] Monomers for the chain radical polymerization include ethylene, 1,3-dienes, styrene (α -methylstyrene), halogenated olefins, vinyl esters, acrylates (methacrylates), acrylonitrile (methacrylonitrile), acrylamide (methacrylamide), N-vinyl carbazole, N-vinyl pyrrolidone. 1-Alkyl olefins, 1,1-dialkyl olefins, vinyl ethers, ketones, and aldehydes cannot undergo the radical chain polymerization.^[3] Albeit any vinyl monomer that will undergo chain radical polymerization is subject to photoinitiated polymerization or photosensitized polymerization, only a few unsaturated monomers are known to absorb light between 250 and 500 nm (i.e., UV-Vis region) which is the most convenient wavelength range for experimental work in the academic research lab or industry. Some monomers, such as vinyl alkyl ketones and vinyl bromide, absorb 300 nm or longer wavelength light and dissociate directly to free radicals which initiated polymerization. Other monomers, such as styrene or methyl methacrylate (MMA), are susceptible to direct photopolymerization on the

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exposure to 300 nm or shorter wavelength light. Although the detailed mechanism of the formation of the propagating radicals in this case is not completely understood, it seems to involve the conversion of an electronically excited singlet state of the monomer to a long-lived excited triplet state.^[4]

Hydrosilanes possess a Si-H bond (bond energy of 323 kJ/mol) that is more reactive than the C-H bond of hydrocarbons (bond energy of 416 kJ/mol).^[5] Hydrosilanes can undergo many interesting reactions: for example, free radical reduction of organic halides,^[6a] nucleophilic reduction of carbonyl compounds,^[6b] dehydrogenative Si-Si coupling,^[7a] and hydrosilation of olefins.^[7b] The last two reactions produce polysilanes and carbosilanes, respectively. The polysilanes with unusual optical and electronic properties due to σ -conjugation along the silicon backbone have been used as ceramic precursors, third-order NLO materials, deep-UV photoresists, photoconductors, and photoinitiators.^[8] The hydrosilation of olefins can be catalyzed either by UV or γ -radiation, peroxides of AIBN (*via* free radical mechanism) or by chloroplatinic acid H_2PtCl_6 or a tertiary base (*via* ionic mechanism). The hydrosilation has been employed to prepare many interesting types of silicon-containing polymers such as dendrimers^[9] and copolymers.^[10] There are few reports on the peroxide- or AIBN-initiated radical polymerization of unsaturated ketones or esters with silanes.^[7b] We first reported the UV-light initiated photopolymerization of MMA with PhSiH_3

to produce poly(MMA)s with hydrosilyl end group.^[11]

In the following sections, this minireview provides selected examples of our recent research developments in photopolymerization of vinyl derivatives in the presence of various initiators such as hydrosilanes, and benzoin silyl ethers. This minireview is not meant to be comprehensive, rather, it is focused on the recent research developments discovered in our laboratory.

1.1. Photopolymerization of vinyl derivatives using hydrosilanes

1.1.1. Hydrosilation

The addition of Si-H bond to unsaturated bonds such as alkenes (including $\text{C}=\text{C}$, $\text{C}=\text{O}$, $\text{C}=\text{metal}$, etc.) and alkynes (including $\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$, $\text{C}\equiv\text{metal}$, etc.) is termed *hydrosilation* (or *hydrosilylation*) and is promoted by many homogeneous transition-metal complex catalysts and heterogeneous supported metal catalysts.^[12] Hydrosilation is an important reaction of forming Si-C bonds in organic chemistry.^[13] The reactions are quite problematic due to many factors such as induction periods, irreproducible kinetics, apparent radical chain processes, olefin isomerization/dimerization, high sensitivity of the products to the nature of the hydrosilating reagent, and obscurity of the real hydrosilation catalysts.^[14] Catalytic hydrosilations are very complex processes and the overall mechanisms are not well understood. Chalk and Harrod proposed a simplified mechanism (Chalk-Harrod mechanism) for tran-

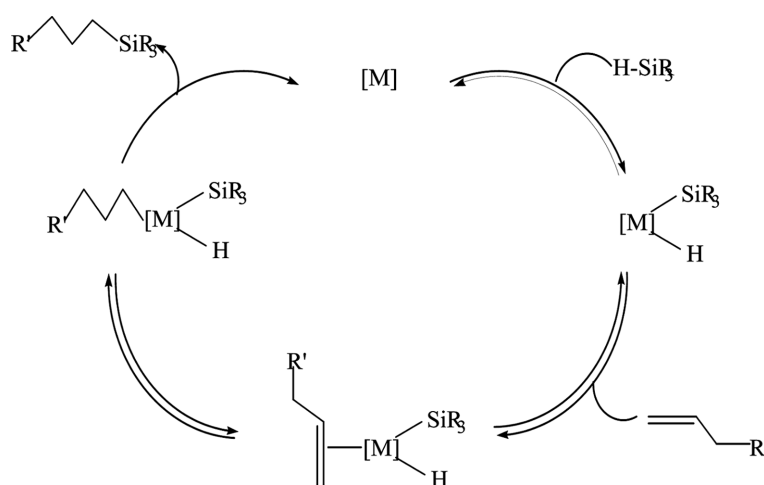


Fig. 1. Chalk-Harrod mechanism for the transition metal complex-catalyzed hydrosilation of olefin.

sition metal complex-catalyzed hydrosilation involving coordination of alkenes to a coordinatively unsaturated transition metal hydride residue, followed by metal-hydride insertion, oxidative addition of the silane to the metal alkyl, then reductive elimination of the alkylsilane to regenerate the metal-hydride (Fig. 1).^[15]

Although the Chalk-Harrod mechanism has been widely accepted,^[16] some phenomena (include an induction period for many precatalysts and the formation of vinylsilanes) cannot be explained well by the Chalk-Harrod mechanism. An alternative mechanism to the Chalk-Harrod mechanism involves insertion of the alkene into the M-Si bond instead of the alkene into the M-H bond.^[17] Alternative mechanisms were also proposed by several researchers on the basis of their studies with their own catalytic systems such as Seitz-Wrighton mechanism (for hydrosilation-dehydrosilation of alkenes), Duckett-Perutz mechanism (for hydrosilation of alkenes catalyzed by Karstedt type of Ni complex), and Brookhard-Grant mechanism (for silyl migration in the hydrosilation catalyzed by cobalt(III) cationic complex where an agostic interaction was involved).^[17,18]

The Yoshida group reported an interesting $\text{RhCl}(\text{PPh}_3)_3$ -catalyzed hydrosilation of alkenes and alkynes using dimethyl(2-pyridyl)silane.^[19] Appreciable hydrosilation of the pyridyl ring of dimethyl(2-pyridyl)silane was not observed from the reaction probably because of its steric bulkiness. In comparison, Woo, Harrod and coworkers reported the hydrosilation-hydrogenation of various pyridine derivatives using Cp_2TiMe_2 catalyst and PhMeSiH_2 as the source of Si-H.^[20] Typically, the reaction is carried out without solvent with a 2:1 molar ratio of silane to pyridine and 10 mol% (based on the mol of pyridine) of Cp_2TiMe_2 , affording hydrogenation-

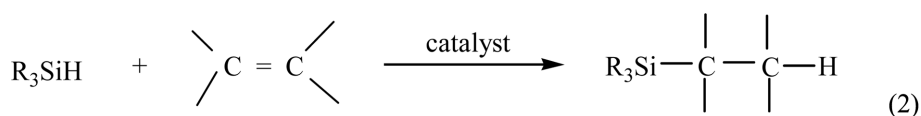
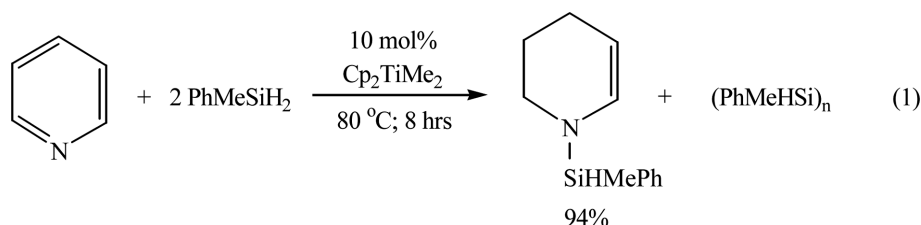
hydrosilation product in 85% yield (eq. 1).^[20a]

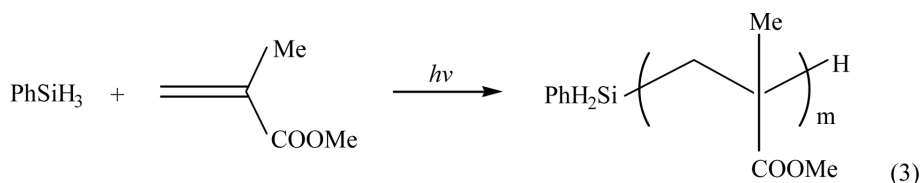
The initial step in the reaction could be the addition of a Ti-Si species across the C=N bond of the pyridine to give an N-silyldihydropyridine. An additional two hydrogen atoms can be transferred to produce the tetrahydropyridine, but complete reduction only occurs in the presence of H_2 . On the other hand, electron-donating substituents and electron-withdrawing substituents on pyridine derivatives affect the reactions in different ways. 3-Picoline with electron-donating substituents gives two hydrogenation-hydrosilation isomers in a 3:2 ratio in 85% yield whereas ethyl nicotinate with electron-withdrawing substituents gives only the hydrosilation product in quantitative yield.^[20b] The reaction rate is strongly dependent on the electronic and steric effects of the substituents. The relative reaction rate decreases in the order of ethyl nicotinate (50) > pyridine (20) > 3-picoline (7) > 4-picoline (3) > 3,5-lutidine (1).^[20b]

1.1.2 Hydrosilaphotopolymerization of methyl methacrylate (MMA) with hydrosilanes

The hydrosilylation of hydrosilanes on olefins (where slight excess of hydrosilane is used) is the single addition of Si-H bond to vinyl derivatives is catalyzed by many soluble transition-metal complexes, free radical initiators, and ultraviolet light (eq. 2).^[12]

As a novel route for synthesizing silicon-containing functional polymer ("silapolyolefin"), we first reported a novel consecutive multiple addition (which has been coined *hydrosilapolymerization by us*) of vinyl monomers to hydrosilanes photochemically to produce the organic polymers with reactive hydrosilyl end groups by the addition of large excess olefin with respect to hydrosilane.^[21]





The bulk hydrosilaphotopolymerization of MMA with primary arylsilane PhSiH_3 and secondary arylsilanes such as PhMeSiH_2 and Ph_2SiH_2 was performed to produce poly(MMA)s containing the corresponding silyl moiety as an end group. Poly(MMA)s possessing the PhSiH_2 moiety as an end group with weight average molecular weight (M_w) of 11000-539000 and TGA residue yields of 10-39% were prepared in 7-92% yields by 300 nm UV light-initiated bulk polymerization of MMA with different molar ratios of PhSiH_3 (MMA : PhSiH_3 = 9:1 through 3:7) as shown (eq. 3).^[11, 21]

It was interestingly found for all the arylsilanes that while the polymer molecular weights and polymerization yields decreased, the TGA residue yields and IR intensities of SiH stretching bands increased with increment of molar ratio of silane over MMA. The polymerization yields increased in the order $\text{PhMeSiH}_2 \leq \text{Ph}_2\text{SiH}_2 < \text{PhSiH}_3$ probably because of steric effect, and the polymer molecular weights and TGA residue yields decreased in the order $\text{PhMeSiH}_2 \geq \text{Ph}_2\text{SiH}_2 > \text{PhSiH}_3$. The bulk photopolymerization of MMA in the absence of the silanes yielded the poly(MMA) with lower polymer molecular weights and TGA residue yield in much lower polymerization yield than that in the presence of silanes, implying that silane act as an initiator. The bulk photopolymerization of MMA with disilane such as 1,2-diphenylsilane and 2-phenyl-1,3-disilapropane was carried out to afford poly(MMA)s containing the corresponding disilyl moiety as an end group. The photopolymerization of MMA with 2-phenyl-1,3-disilapropane produced higher-molecular-weight polymer with lower TGA residue yield when compared to the photopolymerization of MMA with 1,2-diphenyldisilane apparently because of steric effect. The bulk photopolymerization of MMA with various primary alkylsilanes (e.g., benzylsilane, 3-phenoxyphenyl-1-silabutane, 3-naphthyl-1-silabutane, and 3-chlorophenyl-1-silabutane) yielded small amount of silane-free poly(MMA)s. The hydrosilaphotopolymerization yield of MMA with arylsilanes was found to be higher than

those with the alkylsilanes. Thus, the initiating efficiency of arylsilanes is by far higher than that of alkylsilanes.

The bulk photopolymerization of MMA with *para*-substituted phenylsilanes such as *p*-F-C₆H₄SiH₃ (**1**), *p*-H₃C-C₆H₄SiH₃ (**2**), and *p*-H₃CO-C₆H₄SiH₃ (**3**) produces poly(MMA)s containing the respective silyl moiety as an end group. Poly(MMA)s possessing the *p*-F-C₆H₄SiH₂ moiety as an end group with weight average molecular weight (M_w) of 6,200-22,020 and TGA residue yields of 12-73% were prepared in 24-85% yields by 300 nm UV light-initiated bulk polymerization of MMA with different molar ratios of **1** (MMA:1=9:1 through 3:7). Similarly, poly(MMA)s possessing *p*-H₃C-C₆H₄SiH₂ end groups with weight average molecular weights (M_w) of 8,130-28,090 and TGA residue yields of 12-67% were prepared in 30-93% yields by the bulk polymerization of MMA with different molar ratios of **2**. Poly(MMA)s possessing *p*-H₃CO-C₆H₄SiH₂ end groups with weight average molecular weights (M_w) of 6,080-21,100 and TGA residue yields of 18-78% were also prepared in 21-73% yields by the bulk polymerization of MMA with different molar ratios of **3**. For all the hydrosilanes, the polymerization yields and the polymer molecular weights decreased, whereas the TGA residue yields and the relative intensities of Si-H IR stretching bands increased as the relative silane concentration compared to MMA increased. Thus, for all the hydrosilanes the highest polymerization yield and polymer molecular weight were obtained for MMA:hydrosilane = 9:1, but the highest TGA residue yield was obtained for MMA:hydrosilane = 3:7. The polymerization yields and polymer molecular weights of MMA with **1-3** increased in the order of **3** < **1** < **2**.

Weak resonances corresponding to the expected *para*-substituted phenylsilyl end groups appeared, but the resonances corresponding to the potential vinyl end groups were not observed in the ¹H NMR spectra of the poly(MMA)s within detectable limits. One may anti-

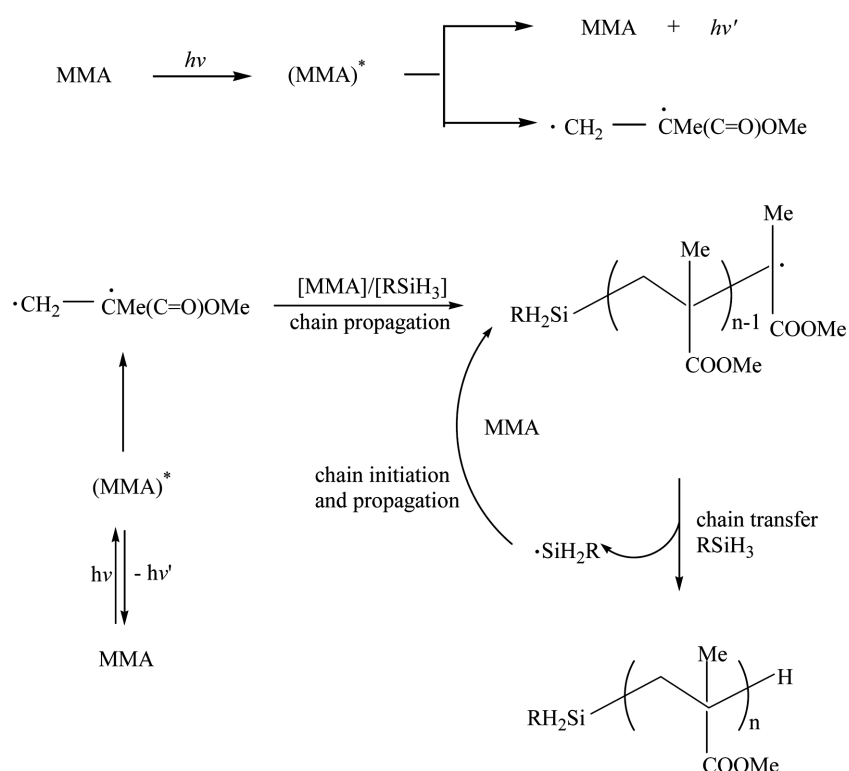


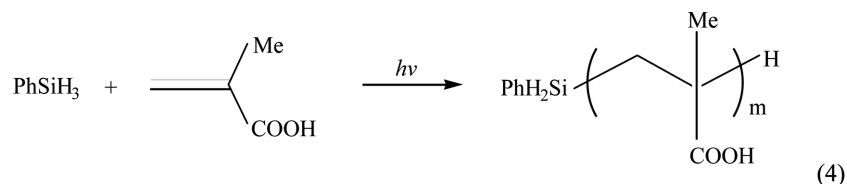
Fig. 2. Potulated mechanism for the photopolymerization of MMA with RSiH_3 .

pate that the silane reactivity (which could be directly related to the hydrogen donation ability of the silane) would increase in the order $1 < 2 < 3$ toward photopolymerization in consideration of only electronic effects because the steric effect of *para*-substituent should be negligible. However, the reactivity order was not observed. The mechanism for the photopolymerization of MMA with PhSiH_3 could be similar to those with other hydrosilanes (Fig. 2).

Light absorption of a MMA molecule is well known to produce an excited singlet state of MMA which may then either fluoresce with a return to the ground state of MMA or may be converted to a long-lived triplet excited state, the diradical of the MMA monomer.^[4] Addition on another MMA by this diradical gives a new diradical of MMA dimer which either reverts to the ground state or continues attacking other MMAs to produce poly(MMA)s. Under neat conditions the latter will be a predominant process to produce poly(MMA) radicals. At high $[\text{MMA}]/[\text{silane}]$ ratios, chain propagation will be able to compete with chain transfer over the

poly(MMA) radicals. However, chain transfer will eventually rule over chain propagation with increasing silane concentration. Chain transfer might produce a silyl radical which, in turn, leads to chain initiation, resulting in the production of poly(MMA) containing silyl end groups. Higher concentrations of hydrosilane over MMA produces shorter chain lengths of poly(MMA), which contributes to the increase in thermal stability of poly(MMA).

Other hydrosilanes similarly exhibit the characteristic trends^[21] as the *p*-substituted phenylsilanes do in the photopolymerization of MMA while the polymer molecular weights and the polymerization yields decline, the relative intensities of Si-H IR stretching bands and the TGA residue yields increase when increasing the silane molar ratio over MMA. The increase of Si-H contents with respect to poly(MMA) moiety will result in the higher possibility of high temperature cross-linking hydrosilation with C=O groups in poly(MMA), which will give higher thermal stability (*i.e.*, higher TGA ceramic residue yield).



1.1.3. Hydrosilaphotopolymerization of methacrylic acid (MA) and acrylic acid (AA) with Hydrosilanes

The bulk photopolymerization of methacrylic acid (MA) with primary arylsilane PhSiH_3 and secondary arylsilane such as PhMeSiH_2 and Ph_2SiH_2 was performed to produce poly(MA)s containing the corresponding silyl moieties. The poly(MA)s with intrinsic viscosities of 0.53-0.99 dL/g and TGA residue yields of 66-69% were prepared in 15-98% yields by bulk photopolymerization of MA with different molar ratio of phenylsilane (MA:phenylsilane = 10:1 though 3:7) (eq. 4).

The polymer were soluble in DMF, DMSO, and methanol. The characterization data of the resulting poly(MA)s are summarized in Table 1.

It is known that high-molecular-weight polymer is formed instantly and that the weight average molecular weight generally increases with increase of polymerization yield in the radical polymerization of vinyl monomers. The intrinsic viscosity is directly related to the weight the polymer. As shown in Table 1, while the polymerization yields and intrinsic viscosities decreased, the relative intensities of SiH IR stretching bands and TGA residue yields increased as the molar ratio of silane over MA augmented. It is worth to note that the intrinsic viscosity and polymerization yield with phenylsilane for the photopolymerization of molar ratio of

MA:phenylsilane = 10:1 were much higher than without phenylsilane. As shown in Table 1, the MA polymerization yields were higher than the MMA polymerization yield. The polymerizability of MA by the silyl radical seems to be naturally higher than that of MMA. The TGA residue yields of poly(MA)s with phenylsilane were much higher than those of poly(MMA)s with phenylsilane. The change of the TGA residue yields of the poly(MA)s with increasing the relative phenylsilane concentration was very little when compared to that of the poly(MMA)s. Interestingly, while the weight loss of the poly(MMA)s was smoothly occurred up to 350°C with few turning points, the abrupt weight loss of a narrow range of the poly(MA)s was occurred twice at the turning points around 150°C and 250°C before 350°C (Fig. 3), although all the poly(MA)s and poly(MMA)s rapidly and exhaustively decomposed after 350°C.

We believe that cross-linking reactions could be happened by the acidolysis between Si-H group and acid group in the different polymer chains at around 150°C, yielding a silyl ester linkage and then by the dehydra-

Table 1. Characterization of Photopolymerization of MA with Phenylsilane^a

Mol ratio (MA:silane)	Yield (%)	Intrinsic Viscosity ^b [η]	Relative intensity ^c IR ($\nu_{\text{Si-H}}$)	TGA residue yield (% at 400 °C)
10:1	98	0.99	1.0	66
7:3	72	0.93	1.2	67
5:5	49	0.87	1.7	68
3:7	15	0.53	2.0	69

^aUV-irradiation for 6 h.

^bMeasured in DMF at 25 °C; unit, dL/g.

^cRelative ratio with respect to the intensity of $\nu_{\text{Si-H}}$ (MA : Phenylsilane=10:1).

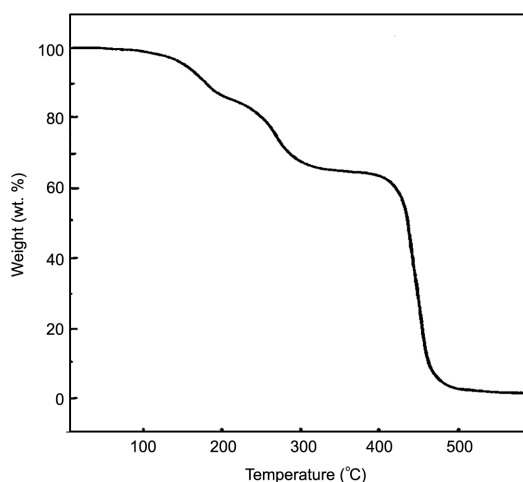


Fig. 3. TGA thermogram of poly(MA) obtained from the photopolymerization of MA with phenylsilane (molar ratio, 10:1).

tion between two acid groups in the different polymer chains at around 250°C, forming an acid anhydride linkage. The little change of the TGA residue yields at 400°C of the poly(MA)s with increasing the relative phenylsilane concentration may suggest that the cross-linking by the formation of acid anhydride linkage should contribute by far more than the cross-linking by the formation of silyl ester linkage. The silyl ester linkage is known to be thermally weak. In consideration of the following items: (1) the trend of solubility, polymerization yields, and intrinsic viscosities with variation of silane concentration and (2) the decrease of hydrogen donation ability of the silyl end group and steric effect exerted by the long alkyl polymer chain, the cross-linking possibility might be slim. The cross-linking processes could require high energy, which are anticipated only to occur during the pyrolysis. However, we should admit at this moment that we cannot completely exclude the low degree of cross-linking possibility.

The hydrosilanes include PhSiH₃, PhCH₂SiH₃, PhMeSiH₂, Ph₂SiH₂, PhSiH₂SiH₂Ph, PhCH(SiH₃)₂, and 1,4-C₆H₄(SiH_{3-x}Me_x)₂. The vinyl monomers include MMA, AA, MA. The hydrosilaphotopolymerization yield of styrene was lower than those of MMA, MA, and AA. No appreciable thermal and photopolymerizations of the vinyl monomers with CH₂(CH₂)₅SiH₃, Ph(CH₂)₂SiH₃, Ph₃SiH, and (mesityl)₂SiH₂ were observed, probably because of their steric and/or electronic effects. Therefore, the types of vinyl monomer and hydrosilane appear to be important for successful hydrosilaphotopolymerization.

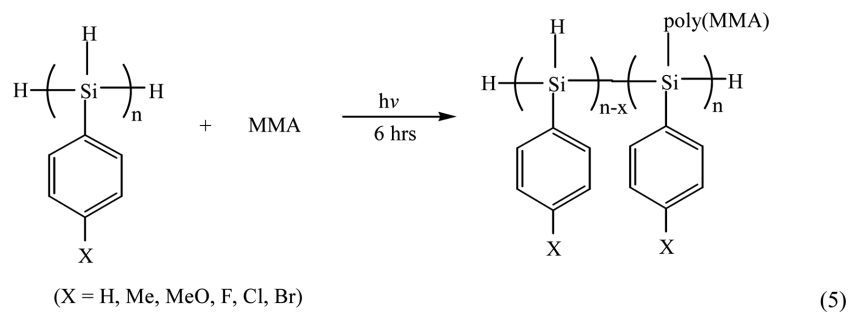
1.1.4. Hydrosilaphotopolymerization of 2-hydroxyethyl methacrylate (HEMA) and styrene with Hydrosilanes

Poly(HEMA)s are widely used for making contact lens. Poly(HEMA) having reactive Si-H end group will be useful to make functional contact lens. The hydrosi-

laphotopolymerization of HEMA and styrene with hydrosilanes were carried out. For HEMA and styrene the similar trends to MMA, MA, AA were found. The hydrosilaphotopolymerization yield of styrene was lower than that of HEMA.^[22] The hydrosilanes include PhSiH₃, PhCH₂SiH₃, PhMeSiH₂, Ph₂SiH₂, PhSiH₂SiH₂Ph, PhCH(SiH₃)₂, and 1,4-C₆H₄(SiH_{3-x}Me_x)₂. No appreciable thermal and photopolymerizations of the vinyl monomers with CH₂(CH₂)₅SiH₃, Ph(CH₂)₂SiH₃, Ph₃SiH, and (mesityl)₂SiH₂ were observed, probably because of their steric and/or electronic effects. Therefore, the types of vinyl monomer and hydrosilane appear to be important for successful hydrosilaphotopolymerization.

1.1.5. Graft hydrosilaphotopolymerization of vinyl monomers on poly(hydrophenylsilane)s to inorganic-organic hybrid polymers

Chatgililoglu and co-workers reported the reactivity study of alkyl peroxy radicals toward poly(hydrosilane)s.^[23] We extended the above consecutive hydrosilylation methodology into poly(arylsilane)s having reactive Si-H in the Si-Si catenated polymer backbone instead of monomeric hydrosilanes in order to make new organic-inorganic hybrid graft copolymer. Thus we first synthesized poly(MMA)s grafted on poly(arylsilane). Poly(*p*-fluoro-substituted phenylsilane), H[(*p*-F-C₆H₄)SiH]_nH, (*M*_w=3300; *M*_w/*M*_n=1.83) was prepared by dehydropolymerization of *p*-F-C₆H₄SiH₃ using the Cp₂ZrCl₂/Red-Al combination catalyst. In a typical photopolymerization experiment, a quartz tube (15 mm×120 mm) charged with MMA, poly(*p*-fluoro-substituted phenylsilane), and toluene (1 mL) was degassed, sealed, and irradiated with UV-light (280 nm) for 6 hours. Precipitation with *n*-hexane, filtration, and drying in vacuo give poly(*p*-fluoro-substituted phenylsilane)-*g*-poly(MMA), which is an inorganic-organic hybrid graft copolymer.



The grafting reaction effectively produced poly(*p*-X-phenylsilane)-*g*-poly(MMA)s (X=H, Me, MeO, F, Cl, Br) (eq. 5).

While the polymerization yields and TGA residue yields of the graft copolymers declined, weight-average molecular weight (M_w) of the polymers increased as the molar ratio of MMA over polysilane augmented. The higher concentration of polysilane over MMA produces the shorter chain length of poly(MMA)s, which, in return, contributes to the enhancement of thermal stability of graft copolymers due to hydrosilylation (crosslinking) between residual SiH bonds and carbonyl bonds (C=O) during the pyrolysis. The average molecular weight and grafting density of polysilane-*g*-poly(MMA) can be controlled by molar ratio of polysilane to MMA. For the other vinyl monomers such as MA and styrene, similar trends are observed.^[24] Similar trends are also observed for the copolymerization of MMA-MA, MMA-styrene, and MA-styrene.^[24] Furthermore, for various other poly(hydroarylsilane)s prepared by $Cp_2MCl_2/Red-Al$ (M = Ti, Zr, Hf) combination catalyst, similar trends are found.^[24]

In brief, poly(*p*-X-phenylsilane)s (X=H, Me, MeO, F, Cl, Br) seem to act as a macromolecular photo-initiator as well as chain transfer agent in the photochemical grafting reaction. Thus, chain initiation and propagation are predominant in high concentration of polysilane, while chain transfer is predominant in high concentration of polysilane. It is well-known that long chain grafting can have dramatic effects on the physical properties of polymers. As poly(MMA)s were grafted on polysilane having Si-H functional groups via photochemical consecutive hydrosilylation, the resulting polymers probably are a star- or comblike polymer. This

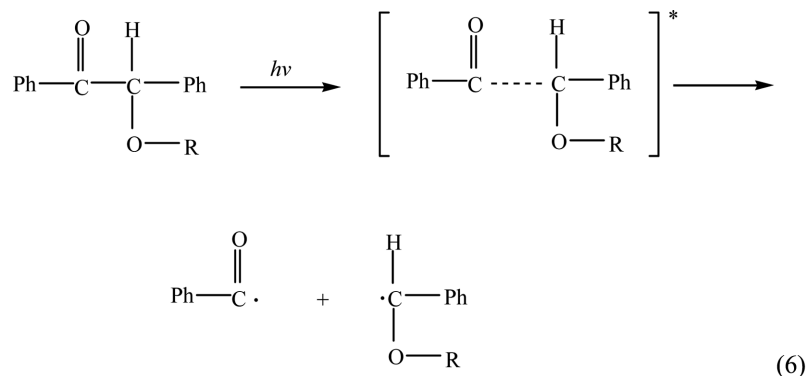
methodology may be extended to other polymeric systems possessing reactive SiH functional groups in order to synthesize new organic-inorganic hybrid nanocomposites.

1.2. Photopolymerization of vinyl derivatives using benzoin and thianthrene cation radical

Intensive studies on the photopolymerization of vinyl monomers initiated by benzoin-derived photoinitiators including benzoin ethers have been made.^[25] We first reported the photopolymerization initiated by benzoin silyl ethers.^[26] The silyl groups of the benzoin silyl ethers have the electron-releasing and sterically bulky natures. The electron-donating ability of the silyl group could help the σ -photocleavage of the benzoin silyl ethers, but its steric bulkiness could deter the attack of the resulting radicals on vinyl monomers.

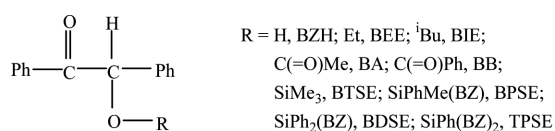
The benzoin silyl ethers such as benzoin trimethylsilyl ether (BTSE), bis(benzoin)phenylmethylsilyl ether (BPSE), bis(benzoin)diphenylsilyl ether (BDSE), and tris(benzoin)phenylsilyl ether (TPSE) are prepared by reacting benzoin with corresponding chlorosilane in the presence of pyridine. The chemical 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 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ and were similar to the those of benzoin esters (i.e., 770 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ for BA and 773 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$ for BB).^[27]

Benzoin alkyl ethers are known to undergo a photocleavage to benzoyl radical and alkoxybenzyl radical as follows (eq. 6):^[28]



Asmus and coworkers reported that α -methoxy benzyl radical independently is photogenerated by H-abstraction from benzyl methyl ether as photoinitiator for MMA polymerization. They claimed that the benzyl radical and benzoyl radical can equally participate in the radical chain propagation of the photopolymerization.^[29]

We have carried out the photopolymerization of 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 the presence and absence of *p*-*tert*-butylcalix[4]arene.



The percent conversion of MMA to poly(MMA) decreases within the experimental error range in the order of BEE > BIE > BTSE \approx BPSE \approx TPSE \approx BZH \approx 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 \geq benzoin ester. 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 Tables 2 and 3.

The order of percent conversion BEE > BIE is due probably to different steric effect imposed by the alkoxy groups. The benzyl radical with ethoxy group from BEE should favor a pyramidal geometry more than that with the isopropoxy group from BIE. Thus, the benzyl radical with ethoxy group can attack on vinyl group of MMA monomer molecular 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 group *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 π - d overlap between vacant d-orbital of Si and filled p-

Table 2. 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 3. 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.

orbital of C.^[30]

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. Very interestingly, as shown in Tables 2 and 3, *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.

Table 4. Solvent Effect on the Photopolymerization of MMA Initiated by BDSE^a

Solvent	Percent conversion ^t	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.

Table 5. Number average molecular weight data of polymerization of vinyl monomers initiated by thianthrene cation radical^a

Monomer	Yield (%)	Mol wt ^b
Styrene	87	2850
Styrene ^c	85	2820
Styrene ^d	55	2690
Ethyl vinyl ether	85	1880
Styrene + Ethyl vinyl ether ^e	85	2200

^aMonomer, 18 mmol; initiator, 0.18 mmol; methylene chloride, 5 mL for 24 h.

^bMeasure with VPO in chloroform.

^cPerformed in the dark.

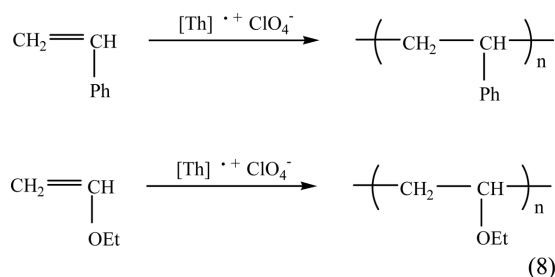
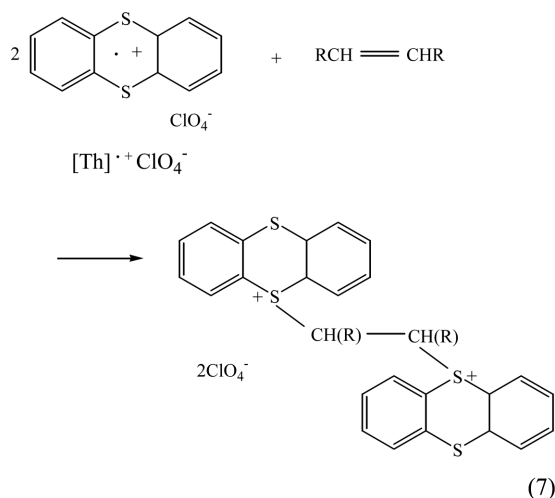
^dPhenylacetylene (0.18 mmol) added.

^e1:1 molar ratio.

The reason is probably because the (n, π^*) transition of the aromatic alcohol groups of the calixarene by 300 nm UV light^[31] and a host-guest interaction between the radicals and calixarene are hardly made. Solvents affected on the photopolymerization of MMA (Table 4).

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 polymer in our study was obtained as shown in Table 3. We do not have the rationalization for this at the present moment.

Thianthrene cation radical perchlorate is a highly reactive species yet having moderate storage life and can react with many agents in a number of ways.^[32] Thianthrene cation radical is reported to just add to



alkenes and alkynes without polymerizing them (eq. 7).^[33]

However, we found that the cation radical can polymerize styrene and ethyl vinyl ether as follow (eq. 8).^[34]

The polymerization in the presence of room light was much faster than that in the dark (2 hrs versus 24 hrs) although the polymer molecular weights of the resulting polymers were similar. The thianthrene cation radical initiated less effectively in the presence of phenylacetylene, as expected (Table 5) because the adduct of thianthrene cation radical to phenylacetylene did not polymerize styrene and ethyl vinyl ether.

2. Conclusions

This miniaccount describes the photopolymerization of vinyl monomers with various organic initiators such as hydrosilanes, poly(hydrosilane)s, benzoin silyl ethers, and thianthrene cation radical. In the photopolymerization of vinyl monomers with silanes, while the polymerization yields and polymer molecular weights of the

poly(MMA)s containing the silyl moieties decreased, the TGA residue yields and intensities of SiH stretching IR bands increased as the mole ratio of the silanes over MMA increased. The photopolymerization yield of MMA with the arylsilane was found to be higher than those with the alkylsilanes and without the silanes. The silyl moieties, once attached to the poly(MMA) as end group, could be left untouched before the pyrolysis occurring at high temperature. The higher contents of Si-H moieties remaining in the graft copolymer backbone will result in the higher possibility of high temperature cross-linking hydrosilation with C=O groups in the graft chain of poly(MMA)s, which will give higher thermal stability (i.e., higher TGA ceramic residue yield). For the other vinyl monomers such as MA, AA, AN, and styrene, similar trends are observed. Furthermore, for various other poly(hydroarylsilane)s prepared by Cp₂MCl₂/Red-Al (M=Ti, Zr, Hf) combination catalyst, similar trends are found in the photo graft copolymerization of vinyl monomers onto poly(hydroarylsilane)s. The silanes and poly(hydrosilane)s appeared to competitively and concurrently function as both chain initiation and transfer agents in the photopolymerization of vinyl monomers. Benzoin silyl ethers and thianthrene cation radical also promote the photopolymerization of MMA.

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