

Photopolymerization of Methyl methacrylate with Phenylsilane

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The photopolymerization of methyl methacrylate (MMA) with phenylsilane was performed. The molecular weights of the poly (MMA) containing SiH moieties were increased with augment of molar ratio of PhSiH₃ over MMA by cross-linking *via* hydrosilation at the expense of isolated yield. Phenylsilane apparently influenced on the photopolymerization as a chain transfer agent and solvent.

Introduction

Light-initiated polymerization of vinyl monomers has received a considerable amount of attention due to its several merits. The most obvious advantages might be the marked convenience and the avoidance of chemical contamination by initiator residues. Photopolymerization technology is used on a commercial scale 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. Some monomers, such as vinyl alkyl ketones and vinyl bromide, absorb 300-nm or longer wavelength light and dissociate directly to free radicals which initiate polymerization. Other monomers, such as styrene or methyl methacrylate, are susceptible to direct photopolymerization on the exposure to 300-nm or shorter wavelength light. Albeit the detailed mechanism of the formation of the propagating radicals in this case is not completely understood, it appears to involve the conversion of an electronically excited singlet state of the monomer to a long-lived excited triplet state.²

Hydrosilanes can undergo dehydrogenative Si-Si coupling³ and hydrosilation⁴ of olefins with catalyst, resulting in the formation of 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.⁵ The hydrosilation of olefins can be catalyzed either by UV or γ -radiation, peroxides or AIBN (*via* free radical mechanism) or by chloroplatinic acid H₂PtCl₆ or a tertiary base (*via* ionic mechanism). The hydrosilation has been used to make many interesting types of silicon containing polymers such as dendrimers⁶ and copolymers.⁷

Many examples for the H₂PtCl₆-catalyzed copolymerization of many unsaturated monomers with various types of silanes are known.⁷ There are few reports on the peroxide- or AIBN-initiated radical polymerization of unsaturated ketones or esters with silanes.⁴ To our knowledge, there is no report to date on the UV-light initiated polymerization of α,β -unsaturated esters with primary silanes.

Various rigid poly(methyl methacrylate) products, such as sheet, rod, and tube, are produced by bulk polymerization

in a casting process. The properties of the polymer can be altered by cross-linking. In the present paper we report the bulk photopolymerization of methyl methacrylate with 300-nm UV light in the presence of PhSiH₃ to give a cross-linked poly(methyl methacrylate).

Experimental Section

General Considerations. 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. Infrared spectra were obtained using a Nicolet 520P FT-IR spectrometer. Proton NMR spectra were recorded on a Bruker ASX 32 (300 MHz) spectrometer using CDCl₃/CHCl₃ as a reference at 7.24 ppm downfield from TMS. 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 Ultrastaygel GPC column series (sequence 500, 10³, 10⁴, 10⁵ 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. Thermogravimetric analysis (TGA) of polymer sample was performed on a Perkin Elmer 7 Series Thermal Analysis System under an air flow. Polymer sample was heated from 25 °C to 700 °C at 20 °C/min. Ceramic residue yield (for convenience at 400 °C) is reported as the percentage of the sample remaining after completion of the heating cycle. For the photolysis experiments Raynot photochemical reactor model RPR-2080, which has merry-go-round system in order to uniformly irradiate all samples, was used. The UV light sources (300 nm; quantum yield = 6.93×10^{18} hv mL⁻¹min⁻¹)⁸ was positioned approximately 17 cm from the reaction quartz tube. The photolysis apparatus was covered completely with wooden chamber such that no UV rays were emitted during photolysis. The heat generated by the lamp caused the internal temperature to increase to 40 °C. AIBN[α,α' -azobis(isobutyronitrile)] was crystallized before use from ethanol. Methyl methacrylate was washed twice with aqueous 5% NaOH (to remove inhibitor), washed twice with distilled water, dried over MgSO₄, and distilled at reduced pressure before use. PhSiH₃ was prepared by reduction of PhSiCl₃ (Aldrich) with LiAlH₄ (Aldrich). Poly(phenylsilane)(M_n = 1450, M_w = 2160, M_w/M_n = 1.5) was prepared according to the literature procedure.³ Poly

(methyl methacrylate)($M_n=8960$, $M_w=10840$, $M_w/M_n=1.2$; TGA ceramic residue yield at 400 °C : 6%) was prepared by photopolymerization of methyl methacrylate using CCl_4 as a photoinitiator in the presence of ferrocene as a trapping agent for chlorine radicals.⁹

Bulk Photopolymerization of Methyl methacrylate with PhSiH_3 . Bulk photopolymerization of methyl methacrylate (MMA) with different molar ratio of PhSiH_3 (10 : 0, 10 : 1, 7 : 3, 5 : 5, and 3 : 7) was carried out. The following procedure is representative of the polymerization reactions. A quartz test tube (1 cm×20 cm) charged with MMA (2.14 mL, 20 mmol) and PhSiH_3 (0.25 mL, 2.0 mmol) was degassed, sealed, and irradiated with UV-light for 6 h. The polymer was taken in toluene, precipitated in hexane, filtered off, and dried to give 1.016 g (92%) of benzene-soluble white solid (TGA ceramic residue yield at 400 °C : 17%). The polymer was characterized by ^1H NMR, IR, GPC, and TGA techniques. IR (KBr cm^{-1}): 2170 w (vSi-H), 1728 s (vC=O), 1070 w (vSi-O). ^1H NMR (δ , CDCl_3 , 300 MHz): 0.7-1.1 (m, 3H, C- CH_3), 1.7-2.1 (m, 2H, CH_2), 3.6 (m, 3H, OCH_3), 5.0-5.3 (m, Si(H)O), 7.2-7.7 (m, ArH). GPC: $M_w=52950$, $M_n=35490$, $M_w/M_n=1.5$. As the molar ratio of PhSiH_3 over MMA increases, the THF-solubility of the polymers decreases. In the presence of excess PhSiH_3 , a hydrosilation product, $\text{PhSi}[\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(=\text{O})\text{OCH}_3]_3$ [IR(KBr pellet, cm^{-1}): 1730 s (vC=O). ^1H NMR (δ , CDCl_3 , 300 MHz): 0.69 (d, $J=7.1$ Hz, 6H, Si- CH_2), 1.15 (d, $J=7.1$ Hz, 9H, CH_3), 2.20 (m, 3H, CH), 3.55 (s, 9H, OCH_3), 7.2-7.8 (m, 5H, ArH)] as an off-white solid was isolated. It should be hence noted that the GPC represents the molecular weight distribution of only THF-soluble portion of the polymers. For comparison, bulk photopolymerization of MMA without PhSiH_3 for 6 h as a control experiment produced a benzene-soluble polymer in small amount after precipitation.

AIBN-Catalyzed Bulk Photopolymerization of MMA with PhSiH_3 . A quartz test tube (1 cm×20 cm) loaded with MMA (2.14 mL, 20 mmol), AIBN (66 mg, 0.4 mmol), and PhSiH_3 (0.25 mL, 2.0 mmol) was degassed, sealed, and irradiated with UV-light for 6 h. The polymer was dissolved in DMF, precipitated in hexane, filtered off, and dried to give 1.05 g (95%) of benzene-insoluble white solid (TGA ceramic residue yield at 400 °C : 20%) with almost no trace of Si-H stretching IR band. The GPC of the polymer could not be obtained due to its low solubility in THF.

Solution Photopolymerization of MMA with PhSiH_3 . A quartz test tube (1 cm×20 cm) was charged with MMA (2.14 mL, 20 mmol), PhSiH_3 (0.25 mL, 2.0 mmol), and benzene (1 mL). The mixture was degassed, sealed, and UV-irradiated for 6 h. The polymer was precipitated in hexane, filtered off, and dried to give 0.11 g (10%) of benzene-soluble white solid. The ^1H NMR and IR spectra were quite similar to those of the polymer above obtained.

Attempted Photoreaction of MMA with Poly(phenylsilane). A quartz test tube (1 cm×20 cm) was loaded with MMA (2.14 mL, 20 mmol), and poly(phenylsilane) (0.32 g, 3.0 mmol equiv.). The mixture was degassed, sealed, and irradiated with UV-light for 6 h. The polymer was precipitated in hexane, filtered off, and dried to give 0.52 g of benzene-soluble white solid which was a mixture of simple hydrosilation adduct of olefinic group of MMA to SiH bonds of the poly(phenylsilane) and small amount of poly(MMA).

Table 1. Photopolymerization of MMA with PhSiH_3 ^a

Mol ratio (MMA : PhSiH_3)	Yield (%)	Mol wt ^b		
		M_w	M_n	PDI ^c
10 : 1	92	52950	35490	1.5
7 : 3	44	22240	14210	1.6
5 : 5	25	12270	7560	1.6
3 : 7	7	10730	8550	1.3

^aUV-irradiation time in neat: 6 h. ^bGPC of only THF-soluble portion of polymer vs polystyrene in THF. ^cPolydispersity index (M_w/M_n).

Table 2. Photopolymerization of MMA with PhSiH_3 ^a

Mol ratio (MMA : PhSiH_3)	Relative intensity ^b IR (ν_{SiH})	TGA residue yield (%, at 400 °C)	Solubility ^c		
			benzene	THF	DMF
10 : 1	1.0	17	MS	S	S
7 : 3	2.0	22	I	MS	S
5 : 5	2.8	31	I	PS	MS
3 : 7	3.3	39	I	PS	MS

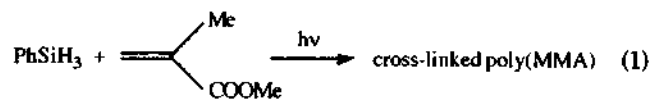
^aUV-irradiation time in neat: 6 h. ^bS: soluble; I: insoluble, MS: mostly soluble, PS: partially soluble. ^cRelative ratio with respect to the intensity of ν_{SiH} (MMA : $\text{PhSiH}_3=10 : 1$).

Attempted Photoreaction of Poly(MMA) with PhSiH_3 . A quartz test tube (1 cm×20 cm) charged with poly(MMA) (2.0 g, 20 mmol equiv.) and PhSiH_3 (0.25 mL, 2.0 mmol) was degassed, sealed, and UV-irradiated for 6 h. The polymer was diluted with benzene, precipitated in hexane, filtered off, and dried to give 1.97 g of benzene-soluble white solid. The product was a poly(MMA) with an NMR, IR, and solubility very similar to those of the starting polymer. Hydrosilation of C=O groups of poly(MMA) appeared not to occur.

Solubility Test. A test tube was charged with 0.05 g of polymer sample and 2 mL of solvent (benzene, chloroform, THF, and DMF, respectively) and agitated at room temperature for 10 h. Solubility was then visually judged.

Results

Bulk Photopolymerization of MMA with PhSiH_3 . The various degree of cross-linked poly(MMA)s were prepared in 7-92% yields by UV (300 nm) light-initiated bulk polymerization of MMA with different molar ratio of PhSiH_3 (10 : 1, 7 : 3, 5 : 5, and 3 : 7) (eq. 1).



The GPC data of the polymers are summarized in Table 1 and the IR, TGA, and solubility data of the polymers are shown in Table 2.

AIBN-Catalyzed Bulk Photopolymerization of MMA with PhSiH_3 . Photopolymerization of MMA with PhSiH_3 (10 : 1 molar ratio) catalyzed by 2 mol% AIBN in neat condition afforded benzene-insoluble white solid in 95% yield with

20% of TGA ceramic residue yield. The GPC of the polymer could not be obtained because of its low solubility in THF. The ^1H NMR and IR spectra apparently showed absence of Si-H bond.

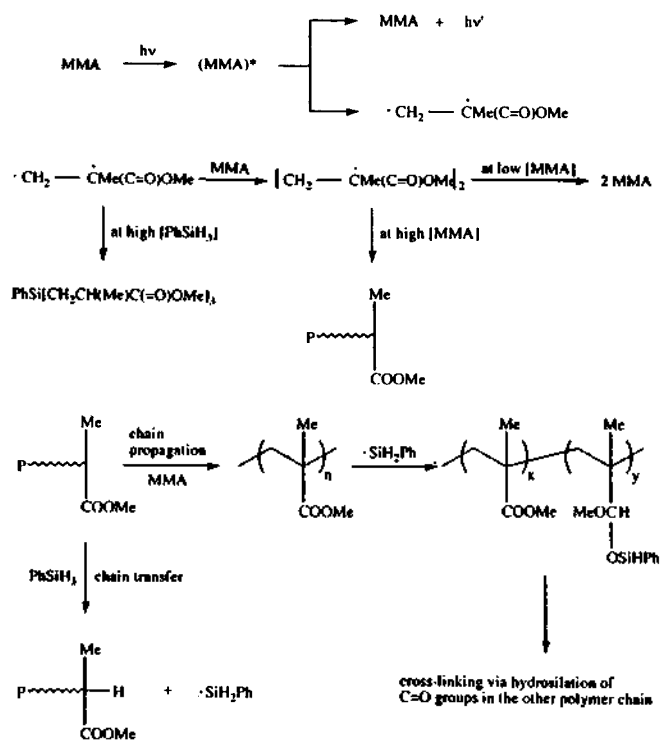
Solution Photopolymerization of MMA with PhSiH_3 . Photopolymerization of MMA with PhSiH_3 (10 : 1 molar ratio) in benzene gave benzene-soluble white solid in 10% yield. The ^1H NMR and IR spectra were quite similar to those of the polymer obtained in the bulk polymerization of MMA with PhSiH_3 (10 : 1 molar ratio).

Attempted Photoreactions. Photoreaction of MMA with poly(phenylsilane) resulted in formation of benzene-soluble white solid which was a mixture of simple hydrosilation adduct of olefinic group of MMA to SiH bonds of the poly(phenylsilane) and small amount of poly(MMA). The starting poly(MMA) was recovered from the photoreaction of poly(MMA) with PhSiH_3 . Hydrosilation of C=O groups of poly(MMA) appeared not to occur.

Discussion

While the isolated yield and solubility of the polymers declined, their relative intensity of SiH stretching IR band and TGA ceramic residue yield augmented in the bulk photopolymerization of MMA as the molar ratio of PhSiH_3 over MMA increased (Table 1 and 2). Although the molecular weights (by GPC) of the polymers diminished with increase of molar ratio of PhSiH_3 over MMA (Table 1), the true molecular weights of the polymers should increase based on their IR, TGA, and solubility data (Table 2) because the GPC represents the molecular weight distribution of only THF-soluble portion of the polymer; the GPC of the insoluble portion of the polymers could not be obtained. The increase of νSiH intensity (*i.e.*, increase of degree of cross-linking) resulted in increase of molecular weights and TGA yield and decrease of solubility. The molecular weight of polymer was increased by adding AIBN, judged by: (1) increase of isolated yield and TGA ceramic residue yield by 3%, (2) decreased solubility, and (3) drastic decrease of the intensity of Si-H stretching IR band. However, when the photopolymerization of MMA was carried out in solution, the polymerization rate and yield significantly decreased.

It is well known that high-molecular-weight polymer is formed immediately in a radical (chain) polymerization.¹ At any instant the reaction mixture contains only monomer, high polymer, and the growing chains. In other words, the molecular weight of the polymer is relatively unchanged during the polymerization, although the overall percent conversion of monomer to polymer increases with reaction time. In the present bulk photopolymerization of MMA with PhSiH_3 , the overall percent conversion of monomer to polymer significantly decreased, but the molecular weight of the polymer increased with augment of PhSiH_3 concentration. This fact can be rationalized as follows (*vide infra*). The absorption of light produces an excited singlet state of MMA which may either fluoresce or be converted to an excited and long-lived triplet excited state, diradical of MMA monomer. Attack on the other MMA by this diradical affords a new diradical of MMA dimer which either reverts to the ground state two MMA molecules or attacks on the other MMA that ultimately initiate polymerization.² At neat condition the latter will be



Scheme 1. Postulated Mechanism for Photoreaction of MMA with PhSiH_3 .

a predominant process to produce poly(MMA) radicals. At high MMA or low PhSiH_3 concentrations, chain propagation will be able to compete with chain transfer over the poly(MMA) radicals. However, the chain transfer will eventually rule over chain propagation with increase of PhSiH_3 concentration. The chain transfer might produce a PhSiH_2 radical which in turn leads to cross-linking by hydrosilation of carbonyl groups of poly(MMA) as shown in Scheme 1.

The hydrosilation of vinyl moiety of MMA in the presence of excess PhSiH_3 will result in retardation of polymerization and formation of a simple hydrosilation product, $\text{PhSi}[\text{CH}_2\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_3]_3$ (characterized by ^1H NMR and IR). PhSiH_3 seems to affect on the photopolymerization as a chain transfer agent and a solvent. Thus, while the percent conversion of MMA to poly(MMA) decreases because of both chain transfer and dilution effects, the molecular weight of the polymer and TGA ceramic residue yield increase because of cross-linking by hydrosilation as the relative PhSiH_3 concentration increases. Although the chain transfer constant of PhSiH_3 for radical polymerization of MMA is not available, PhSiH_3 could be an excellent chain transfer agent because PhSiH_3 has low Si-H bond energy of 88.2 kcal/mol¹⁰ which is comparable to S-H bond energy of 87 kcal/mol.¹¹ Mercaptans are known to date to be one of most powerful chain transfer agents. In fact, it has been reported that chain transfer constant for radical polymerization of MMA at 60 °C is 2.7 for thiophenol and 0.12 for triphenylsilane.¹²

The smaller silane should be better for the cross-linking of poly(MMA), and the cross-linking process could occur *via* a radical process. The facts are well illustrated by the following experiments: (1) photoreaction of MMA with poly(phenylsilane) yielded the product mixture of simple hydrosilatiln

adduct of olefinic group of MMA to SiH bonds of the poly(phenylsilane) and small amount of poly(MMA) and (2) no photoreaction of poly(MMA) with PhSiH₃ took place.

In conclusion, this work describes the photopolymerization of MMA with phenylsilane. The molecular weights of the poly(MMA) containing Si-H moieties are increased as the molar ratio of PhSiH₃ over MMA increased by cross-linking via hydrosilation of Si-H bond to C=O group of the polymer, but the isolated yield is in turn decreased. This is supported by the spectroscopic and solubility data and some reaction chemistry. AIBN accelerates the polymerization reaction rate and increases molecular weights. Phenylsilane seems to function as a chain transfer agent and solvent.

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Hydroiminoacylation of Allyl and Homoallyl Alcohol Derivatives with Benzaldimine and Solvolysis of Hydroacylated Products

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Hydroiminoacylations of allyl and homoallyl alcohol and their derivatives with benzaldimine by Wilkinson's complex have been studied. All these terminal alkene derivatives except allyl alcohol were hydroacylated according to anti-Markownikoff's rule to give the corresponding linear alkyl compounds without showing oxygen directing effect, even though hydroiminoacylation of 3-acetoxy-1,5-hexadiene showed strong allyloxy directing effect over homoallyloxy directing effect in a 92 : 8 ratio. Solvolysis of 4-acetoxy-1-phenylbutan-1-one, previously prepared by hydroiminoacylation, in ethanol led to etherification giving 4-ethoxy-1-phenylbutan-1-one through neighbouring group participation, while that of 5-acetoxy-1-phenylpentan-1-one led to common transesterification giving 5-hydroxy-1-phenylpentan-1-one. Application of branched alkanols such as isopropanol and *t*-butanol in solvolysis of 4-acetoxy-1-phenylbutan-1-one underwent competition between etherification and transesterification.

Introduction

Hydroacylation is one of interesting reactions in organo-

metallic chemistry since ketone can be directly synthesized from olefin and aldehyde by organotransition metal catalyst.¹ However, decarbonylation of aldehyde is one of major side