

Photopolymerization of Methyl Methacrylate with Secondary Silanes

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The photopolymerization of methyl methacrylate (MMA) with secondary silane (PhMeSiH_2 and Ph_2SiH_2) was carried out to produce poly(MMA)s containing silane moieties. While the molecular weights and polymerization yields decreased, the TGA residue yields and IR $\nu_{\text{Si-H}}$ relative intensities increased with augmentation of molar ratio of silane over MMA. The sterically less bulky silane PhMeSiH_2 afforded poly(MMA)s having somewhat higher molecular weights and TGA residue yields than the sterically bulkier silane Ph_2SiH_2 . The silanes seemed to influence on the photopolymerization as both chain initiation and chain transfer agents.

Introduction

Polymerization of vinyl monomers initiated by light has been given a great amount of attention due to its several merits. The most distinct advantages might be the outstanding 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 Albeit 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 (MMA), are susceptible to direct photopolymerization on the exposure to 300 nm or shorter wavelength light. Although the minute 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.²

Hydrosilanes can undergo many interesting reactions: for example, free radical reduction of organic halides,^{3a} nucleophilic reduction of carbonyl compounds,^{3b} dehydrogenative Si-Si coupling,^{4a} and hydrosilation of olefins with catalyst.^{4b} 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.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 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 dendrimers⁶ and copolymers.⁷

There are few reports on the peroxide- or AIBN-initiated radical polymerization of unsaturated ketones or esters with silanes.^{4b} We recently reported the UV-light initiated polymerization of α,β -unsaturated ester MMA with PhSiH_3 .⁸ One

may anticipate that the sterically more bulky secondary silanes will show somewhat different reaction mode from the sterically less bulky primary silane PhSiH_3 . Various rigid poly(MMA) products, such as sheet, rod, and tube, are produced by bulk polymerization in a casting process. The properties of the polymer can be easily altered by adding some functional groups to the polymer chain. In the present paper we report the bulk photopolymerization of MMA with 300 nm UV light in the presence of secondary silanes R_2SiH_2 to give a poly(MMA) containing silane moiety to be readily converted to various functional groups by some chemical modifications which will, in turn, endow new physical properties.

Experimental Section

Materials and Instrumentation. 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 $\text{CDCl}_3/\text{CHCl}_3$ 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 Ultrastyrigel GPC column series (sequence 10^3 , 10^4 , 10^5 , 10^6 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 a nitrogen flow (50 mL/min). Polymer sample was heated from 25 °C to 700 °C at 10 °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 a Raynot photochemical reactor model RPR-2080 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 inten-

Table 1. GPC Characterization of Photopolymerization of MMA with Secondary Silanes^a

Silane	Mol ratio (MMA : Silane)	Yield (%)	Mol wt ^b		
			M_w	M_n	PDI ^c
PhMeSiH ₂	10 : 1	29	161000	63000	2.6
	7 : 3	25	33000	16000	2.1
	5 : 5	20	18000	10000	1.8
	3 : 7	7	11000	7000	1.6
Ph ₂ SiH ₂	10 : 1	31	106000	42000	2.5
	7 : 3	23	28000	15000	1.9
	5 : 5	11	16000	10000	1.6
	3 : 7	6	8000	6000	1.3
no silane	10 : 0	5	8000	6000	1.3

^aUV-irradiation for 6 h. ^bMeasured with GPC in THF. ^cPolydispersity index (M_w/M_n).

sity = 6.93×10^{18} hv mL⁻¹ min⁻¹⁹ 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. MMA 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. PhMeSiH₂ and Ph₂SiH₂ were prepared by reduction of PhMeSiCl₂ and Ph₂SiCl₂ (Aldrich Chemical Co.) with LiAlH₄ (Aldrich Chemical Co.).

Bulk Photopolymerization of MMA with PhMeSiH₂.

Bulk photopolymerization of MMA with different molar ratio of PhMeSiH₂ (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 PhMeSiH₂ (0.27 mL, 2.0 mmol) was degassed, sealed, and irradiated with UV-light for 6 h. The polymer was precipitated in hexane, filtered off, and dried to give 0.65 g (29%) of white solid (TGA residue yield at 400 °C: 14%). The polymer was totally soluble in THF and benzene, and was characterized by ¹H NMR, IR, GPC, and TGA techniques. IR (KBr pellet, cm⁻¹): 2170 w (νSi-H), 1720 s (νC=O). ¹H NMR (δ, CDCl₃, 300 MHz): 0.2-0.5 (m, Si-CH₃), 0.7-1.1 (m, 3H, C-CH₃), 1.7-2.1 (m, 2H, CH₂), 3.6 (m, 3H, OCH₃), 4.2-4.5 (m, SiH), 7.2-7.7 (m, ArH). GPC: M_w = 161000, M_n = 63000, M_w/M_n = 2.6. For comparison, bulk photopolymerization of MMA without PhMeSiH₂ for 6 h as a control experiment produced a benzene-soluble polymer (0.10 g, 5%). TGA ceramic residue yield at 400 °C: 3%; GPC: M_w = 8000, M_n = 6000, M_w/M_n = 1.3.

Bulk Photopolymerization of MMA with Ph₂SiH₂.

Bulk photopolymerization of MMA with different molar ratio of Ph₂SiH₂ (10 : 1, 7 : 3, 5 : 5, and 3 : 7) was performed. The following procedure is a typical example of the polymerization reactions. A quartz test tube (1 cm × 20 cm) was loaded with MMA (2.14 mL, 20 mmol) and Ph₂SiH₂ (0.37 mL, 2.0 mmol). The mixture was degassed, sealed, and UV-irradiated for 6 h. The polymer was precipitated in hexane, filtered off, and dried to give 0.73 g (31%) of white solid (TGA residue yield at 400 °C: 12%). The polymer was readily soluble in benzene and THF, and was characterized by ¹H

Table 2. Photopolymerization of MMA with Secondary Silanes^a

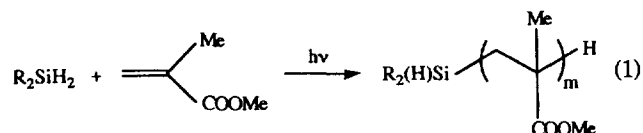
Silane	Mol ratio (MMA : Silane)	Relative intensity ^b	TGA residue yield
		IR (ν _{SiH})	(%, at 400 °C)
PhMeSiH ₂	10 : 1	1.0	14
	7 : 3	1.9	43
	5 : 5	2.7	50
	3 : 7	3.2	56
Ph ₂ SiH ₂	10 : 1	1.0	12
	7 : 3	2.0	39
	5 : 5	3.0	48
	3 : 7	3.4	51
no silane	10 : 0	0	3

^aUV-irradiation for 6 h. ^bRelative ratio with respect to the intensity of ν_{SiH} (MMA : Silane = 10 : 1).

NMR, IR, GPC, and TGA techniques. IR (KBr pellet, cm⁻¹): 2140 w (νSi-H), 1710 s (νC=O). ¹H NMR (δ, CDCl₃, 300 MHz): 0.7-1.1 (m, 3H, C-CH₃), 1.7-2.1 (m, 2H, CH₂), 3.6 (m, 3H, OCH₃), 4.6-4.9 (m, SiH), 7.2-7.8 (m, ArH). GPC: M_w = 106000, M_n = 42000, M_w/M_n = 2.5.

Results and Discussion

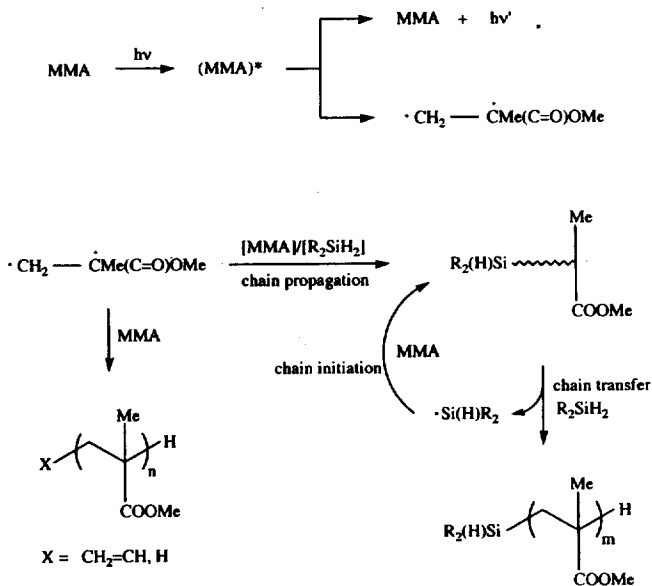
Bulk Photopolymerization of MMA with Secondary Silane. The poly(MMA)s containing silane moieties were prepared in 6-31% yields by UV (300 nm) light-initiated bulk polymerization of MMA with different molar ratio of the secondary silane (MMA : silane = 10 : 1, 7 : 3, 5 : 5, and 3 : 7) such as PhMeSiH₂ and Ph₂SiH₂ (eq. 1).



The polymerization yields and GPC data of the polymers are summarized in Table 1 and the IR and TGA data of the polymers are given in Table 2.

While the polymerization yields and molecular weights of the polymers decreased, their relative intensities of Si-H stretching IR bands and TGA residue yields increased in the bulk photopolymerization of MMA as the molar ratio of R₂SiH₂ over MMA augmented. The TGA residue yields and molecular weights of the polymers with PhMeSiH₂ were found to be somewhat higher than with Ph₂SiH₂. It is well known that the weight average molecular weight generally increases with increase of polymerization yield in the radical polymerization.¹

It is well known that high-molecular-weight polymer is formed instantly 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 polymerization yield increases with reaction time. In the present bulk photopoly-



Scheme 1. Postulated Mechanism for Photoreaction of MMA with R_2SiH_2 .

merization of MMA with R_2SiH_2 , the molecular weight of the polymer and polymerization yield significantly decreased with increase of R_2SiH_2 concentration. It should be also noted that the molecular weight of the polymer and polymerization yield with silane were much higher than without silane for the photopolymerization of molar ratio of MMA : $\text{R}_2\text{SiH}_2 = 10 : 1$. In other words, the silane helped the photopolymerization of MMA up to a molar ratio of MMA : silane of 10, but hampered the reaction after the molar ratio with increase of the silane concentration.¹⁰ While ^1H NMR spectra of both poly(MMA) and poly(MMA)s containing silane moieties (up to the molar ratio of MMA : silane of 10) exhibited the presence of vinyl end groups, ^1H NMR spectra of poly(MMA) prepared from smaller molar ratio of MMA : silane than 10 showed absence of vinyl end groups.¹⁰ These facts can be rationalized as follows (*vide infra*). The absorption of light produces an excited singlet state of MMA which may either be fluoresced 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 a predominant process to produce poly(MMA) radicals. At high MMA or low R_2SiH_2 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 R_2SiH_2 concentration. The chain transfer might produce a R_2SiH radical which, in turn, leads to chain initiation, resulting in the production of poly(MMA) containing the silane moiety as an end group as shown in Scheme 1.

The hydrosilation of vinyl moiety of MMA in the presence of excess R_2SiH_2 will result in retardation of polymerization.⁸ R_2SiH_2 seems to affect on the photopolymerization as both chain initiation and chain transfer agents. Thus, the molecu-

lar weights of polymers and polymerization yields increased, reached the peak at the molar ratio of MMA : $\text{R}_2\text{SiH}_2 = 10 : 1$ and then decreased, but the TGA residue yields decreased, reached bottom at the molar ratio and then increased as the relative R_2SiH_2 concentration increases. The reason is probably because both chain initiation and chain transfer competitively operate at the same time. Although the chain transfer constant of R_2SiH_2 for radical polymerization of MMA is not available, R_2SiH_2 could be an excellent chain transfer agent because PhSiH_3 has low Si-H bond energy of 88.2 kcal/mol¹¹ which is comparable to S-H bond energy of mercaptans, known to date to be one of most powerful chain transfer agents, of 87 kcal/mol.¹² 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.¹³ The steric effect of silane could be important in the chain initiation and transfer processes. Thus, the sterically smaller silane PhMeSiH_2 should be better than the larger silane Ph_2SiH_2 for the chain initiation and transfer processes. As a matter of fact, the photopolymerization of MMA with PhSiH_3 bestowed the polymers in much higher polymerization yields than with R_2SiH_2 .⁸ However, the electronic effect of the silanes seemed not to be important because the Si-H bond energies of silanes are known to be mostly uniform except the silanes with strongly electron-withdrawing and/or silyl substituents.^{3a} The poly(phenylsilane) expected to have low Si-H bond energy^{3a} did not initiate the photopolymerization of MMA, and poly(MMA) did not photochemically react with hydrosilane.⁸ Therefore, one can assume that the silane moieties R_2SiH , once attached to the poly(MMA), could contribute significantly to increase TGA residue yield during pyrolysis without further participation in the chain initiation and transfer processes of the photopolymerization of MMA.

In conclusion, this work describes the photopolymerization of MMA with secondary silane such as PhMeSiH_2 and Ph_2SiH_2 . While the polymerization yields and molecular weights of the poly(MMA) containing Si-H moieties decreased, TGA residue yields increased as the molar ratio of R_2SiH_2 over MMA increased. This fact implies that the silane moieties, once attached to the poly(MMA) as end group, could be left untouched until the pyrolysis occurring at high temperature. The smaller silane PhMeSiH_2 afforded poly(MMA)s having somewhat higher molecular weights and TGA residue yields than the larger silane Ph_2SiH_2 . The secondary silanes appeared to competitively function as both chain initiation and transfer agents in the photopolymerization of MMA.

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