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## Polymerization of Methyl Methacrylate with Phenylsilane

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The bulk thermal and photopolymerization of methyl methacrylate (MMA) with phenylsilane were performed to produce poly(MMA)s containing phenylsilyl moiety presumably as an end group. It was found for both thermal and photopolymerization that while the polymerization yields and polymer molecular weights decreased as the relative phenylsilane concentration increases, the TGA residue yields and the relative intensities of SiH IR stretching bands increased with increasing molar ratio of phenylsilane over MMA. The polymerization yield, molecular weight, and TGA residue yield for the thermal polymerization were higher than those for the photopolymerization. Thus, the phenylsilane seemed to significantly influence on the polymerization as both chain initiation and chain transfer agents. However, an appreciable silane effect was not observed on the thermal and photopolymerization of 4-vinylpyridine, acrylonitrile, styrene, and vinyltrimethoxysilane.

### Introduction

A wide variety of unsaturated vinyl derivatives can be induced to undergo free-radical chain polymerization.<sup>1</sup> The capability to carry out a thermodynamically feasible polymerization relies on its kinetic feasibility on whether the process proceeds at a reasonable rate under a given set of reaction conditions. Initiator or promotor are often required to achieve the kinetic feasibility. Photopolymerization technology applicable conveniently is widely employed on a commercial scale today in the areas of surface coatings, photoresists, adhesives, and holography.<sup>1</sup> Although any vinyl monomer that will undergo chain polymerization is basically subject to photopolymerization or photosensitized polymerization, only a few unsaturated monomers are known to absorb 250-500 nm wavelength light which is the most convenient wavelength range for experimental work. The detailed mechanism of the formation of the propagating radicals in this case is not thoroughly understood, but it appears to involve the conversion of an electronically excited singlet state of the monomer to a long-lived excited triplet state.<sup>2</sup>

Hydrosilane is known to participate in versatile reactions such as free radical reduction of organic halides,<sup>3</sup> nucleophilic reduction of carbonyl compounds,<sup>4</sup> dehydropolymerization,<sup>5</sup> cross-dehydrocoupling,<sup>6</sup> and hydrosilation of olefins<sup>7</sup> with catalyst. The hydrosilation has been used to prepare many intriguing types of silicon containing polymers such as dendrimers<sup>8</sup> and copolymers.<sup>9</sup> We reported the bulk photopolymerization of methyl methacrylate (MMA) with various silanes.<sup>10</sup> Here we wish to report the bulk thermal and photopolymerization of MMA with phenylsilane to give poly

(MMA)s containing phenylsilyl moiety presumably as an end group. We also describe the silane effect on the bulk thermal and photopolymerization of various vinyl derivatives.

### 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 under the same conditions such as cell thickness, sample concentration, etc. using a Nicolet 520P FT-IR spectrometer. Proton NMR spectra were recorded on a Bruker ASX 32 (300 MHz) spectrometer using CDCl<sub>3</sub>/CHCl<sub>3</sub> 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 Ultrasyrage GPC column series (sequence 10<sup>3</sup>, 10<sup>4</sup>, 10<sup>5</sup>, 10<sup>6</sup> 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). The polymer sample was heated from 25 to 700 °C at a rate of 10 °C/min. TGA residue yield (as a matter of convenience, read 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 intensity =  $6.93 \times 10^{18}$  hv mL<sup>-1</sup> min<sup>-1</sup>) was positioned approximately 17 cm from the reaction quartz tube. For the thermal polymerization experiments a thermostat bath (model SVM-67) made by the Samik Scientific Co. was used. Methyl methacrylate and styrene (Aldrich Chemical Co.) were washed with aqueous 5% sodium hydroxide (to remove inhibitor), washed with distilled water, dried over magnesium sulfate, and distilled at reduced pressure before use. Acrylonitrile (Aldrich Chemical Co.) was washed with dilute sulfuric acid, washed with aqueous sodium carbonate, dried over magnesium sulfate, and distilled before use. Vinyltrimethoxysilane and 4-vinylpyridine (Aldrich Chemical Co.) were distilled at reduced pressure before use. PhSiH<sub>3</sub> was prepared by reduction of PhSiCl<sub>3</sub> (Hüls America Inc.) with LiAlH<sub>4</sub> in diethyl ether.<sup>11</sup>

**Bulk Photopolymerization of MMA with Phenylsilane.** Bulk photopolymerization of MMA with different molar ratio of PhSiH<sub>3</sub> (10 : 1 through 3 : 7) was carried out. The following procedure is the representative of the photopolymerization reactions. A quartz test tube (1 cm × 20 cm) charged with MMA (2.0 g, 20 mmol) and PhSiH<sub>3</sub> (0.22 g, 2.0 mmol) was degassed, sealed, and irradiated with 300 nm UV-light for 6 h. The polymer was taken in toluene, precipitated in hexane, filtered off, and dried to give 2.03 g (92%) of benzene-soluble white solid (TGA residue yield at 400 °C : 17%). The polymer was characterized by <sup>1</sup>H NMR, IR, GPC, and TGA techniques. IR (KBr pellet, cm<sup>-1</sup>): 2170 w (ν<sub>Si-H</sub>), 1728 s (ν<sub>C=O</sub>). <sup>1</sup>H NMR (δ, CDCl<sub>3</sub>, 300 MHz): 0.7-1.1 (m, 3H, C-CH<sub>3</sub>), 1.7-2.1 (m, 2H, CH<sub>2</sub>), 3.6 (m, 3H, OCH<sub>3</sub>), 4.0-4.3 (m, SiH), 5.6, 6.1 (br, H<sub>2</sub>C=), 7.2-7.7 (m, ArH). GPC:  $M_w = 53000$ ,  $M_n = 35000$ . As a control experiment, bulk photopolymerization of MMA without PhSiH<sub>3</sub> for 6 h produced poly(MMA) in small amount after precipitation.

**Bulk Thermal Polymerization of MMA with Phenylsilane.** Bulk thermal polymerization of MMA with different molar ratio of PhSiH<sub>3</sub> (10 : 1 through 3 : 7) was performed. In a typical experiment, a test tube (1 cm × 20 cm) loaded with MMA (2.0 g, 20 mmol) and PhSiH<sub>3</sub> (0.22 g, 2.0 mmol) was degassed, sealed, and heated at 70 °C for 6 h. The polymer was dissolved in toluene, precipitated in hexane, filtered off, and dried to afford 1.89 g (86%) of benzene-soluble white solid (TGA residue yield at 400 °C : 33%). The polymer was characterized by <sup>1</sup>H NMR, IR, GPC, and TGA techniques. The IR and <sup>1</sup>H NMR spectra were quite similar to the IR and <sup>1</sup>H NMR spectra of the poly(MMA) obtained from the photopolymerization. GPC:  $M_w = 60000$ ,  $M_n = 25000$ . In contrast, bulk thermal polymerization of MMA without PhSiH<sub>3</sub> at 70 °C for 6 h yielded poly(MMA) in small amount after precipitation.

**Bulk Polymerization of Other Vinyl Derivatives with Phenylsilane.** Bulk photopolymerization of several vinyl monomers with fixed molar ratio of PhSiH<sub>3</sub> (monomer : phenylsilane = 10 : 1) was carried out. The following procedure is the representative of the photopolymerization reactions. A quartz test tube (1 cm × 20 cm) charged with 4-vinylpyridine (2.1 g, 20 mmol) and PhSiH<sub>3</sub> (0.22 g, 2.0 mmol) was degassed, sealed, and irradiated with 300 nm UV-light for 6 h. The polymer was obtained in small amount after

**Table 1.** Characterization of Photopolymerization of MMA with Phenylsilane<sup>a</sup>

Mol ratio (MMA : Silane)	Yield (%)	Mol wt <sup>b</sup>		Relative intensity <sup>c</sup> IR (ν <sub>SiH</sub> )	TGA residue yield (%, at 400 °C)
		$M_w$	$M_n$		
10 : 1	92	53000	35000	1.0	17
7 : 3	44	22000	14000	2.0	22
5 : 5	25	12000	8000	2.8	31
3 : 7	7	11000	9000	3.3	39

<sup>a</sup>UV-irradiation for 6 h. <sup>b</sup>Measured with GPC in THF. <sup>c</sup>Relative ratio with respect to the intensity of ν<sub>SiH</sub> (MMA : Phenylsilane = 10 : 1).

**Table 2.** Characterization of Thermal Polymerization of MMA with Phenylsilane<sup>a</sup>

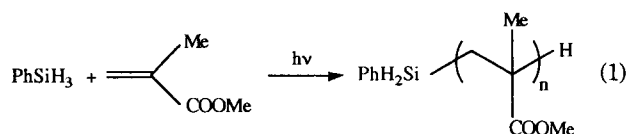
Mol ratio (MMA : Silane)	Yield (%)	Mol wt <sup>b</sup>		Relative intensity <sup>c</sup> IR (ν <sub>SiH</sub> )	TGA residue yield (%, at 400 °C)
		$M_w$	$M_n$		
10:1	86	60000	25000	1.0	33
7:3	75	30000	12000	2.1	40
5:5	55	20000	9000	2.9	51
3:7	32	17000	7000	3.5	58

<sup>a</sup>Heating at 70 °C for 6 h. <sup>b</sup>Measured with GPC in THF. <sup>c</sup>Relative ratio with respect to the intensity of ν<sub>SiH</sub> (MMA : Phenylsilane = 10 : 1).

precipitation. The photopolymerization of acrylonitrile, styrene, and vinyltrimethoxysilane yielded the same results. Similarly, an appreciable silane effect was not observed on the thermal polymerization of the vinyl monomers at 70 °C.

## Results and Discussion

The poly(MMA)s containing phenylsilyl moiety with weight average molecular weights of 11000-53000 and TGA residue yields of 17-39% were prepared in 7-92% yields by bulk photopolymerization of MMA with different molar ratio of phenylsilane (MMA : phenylsilane = 10 : 1 through 3 : 7) (eq. 1).



The characterization data of the obtained poly(MMA)s are summarized in Table 1.

The poly(MMA)s possessing phenylsilyl moiety with weight average molecular weights of 17000-60000 and TGA residue yields of 33-58% were synthesized in 32-86% yields by bulk thermal polymerization of MMA with varying the molar ratio of phenylsilane (MMA : phenylsilane = 10 : 1 through 3 : 7). The characterization data of the resulting poly(MMA)s are given in Table 2.

It is well known that high-molecular-weight polymer is formed immediately and that the weight average molecular weight generally increases with increase of polymerization

yield in the radical polymerization of vinyl monomers.<sup>1</sup> As shown in Table 1 and 2, for both thermal and photopolymerization while the polymerization yields and polymer molecular weights decreased, the relative intensities of SiH IR stretching bands and TGA residue yields increased as the molar ratio of silane over MMA augmented. It should be also noted that the molecular weight of the polymer and polymerization yield with phenylsilane for the photopolymerization of molar ratio of MMA : silane = 10 : 1 were much higher than without phenylsilane. In other words, the phenylsilane apparently helps the photopolymerization of MMA until the molar ratio of MMA : phenylsilane reaches at 10, but to hamper the reaction after the molar ratio with increase of the phenylsilane concentration. The polymerization yield, molecular weight, and TGA residue yield for the thermal polymerization were generally higher than those for the photopolymerization. These facts can be rationalized as follows (*vide infra*). The absorption of light or heat may produce an excited singlet state of MMA which will 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.<sup>2</sup> At neat condition the latter will be a predominant process to produce poly(MMA) radicals. At high MMA or low silane 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 silane concentration. The chain transfer might produce a silyl radical which, in turn, leads to chain initiation, resulting in the production of poly(MMA) containing the silyl moiety as an end group.<sup>10</sup> The polysilyl radicals generated from the photochemical homolysis of polysilanes are known to initiate the free-radical chain polymerization of some vinyl monomers.<sup>12</sup> The phenylsilane seems to affect on the thermal and photopolymerization as both chain initiation and chain transfer agents by operating competitively and simultaneously. Although the direct chain transfer constants of the phenylsilane for radical polymerization of MMA are not available, it could serve as an excellent chain transfer agent because PhSiH<sub>3</sub> has low Si-H bond energy of 88.2 kcal/mol<sup>13</sup> 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.<sup>14</sup> 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.<sup>15</sup> In the present study we used phenylsilane which is an arylsilane without methylene spacer between phenyl group and silicon center. We described the photopolymerization of MMA with aryl substituted alkylsilane, 3-aryl-1-silabutanes because we wanted to check the effect of aryl group on the photopolymerization.<sup>10b</sup> The effect of the aryl group of substituted alkylsilane turned out to be negligible. Photopolymerization of MMA with alkylsilanes also produced the corresponding poly(MMA)s in very low yields. The polymerization yield of MMA with the alkylsilanes was found to be much lower than those with the arylsilane, phenylsilane although the Si-H bond energies of silanes are known to be mostly uniform except the silanes with strongly electron-withdrawing and/or silyl substituents in the  $\alpha$ -position.<sup>3a</sup> It is

recently reported that the substitution of methyl group on the silicon atom decreases the hydrogen donation ability of the silane, but the substitution of phenyl group increases it.<sup>16</sup> The hydrogen donation ability of a silane appears to be not related always to the Si-H bond energy of a silane. This might suggest that the aryl group first receives the energy and then transfers it into the silicon center, which leads to the homolysis of Si-H bond. The energy transmission could be at short range. However, we are not sure of this hypothesis yet. A study for verifying the matter is in progress using fluorophotometer. We are also uncertain whether the thermal polymerization of MMA proceeds through the same path. The silane effect was tested on the bulk thermal and photopolymerization of several vinyl monomers with fixed molar ratio of phenylsilane (monomer : phenylsilane = 10 : 1). A similar silane effect appeared on the thermal and photopolymerization of methacrylic acid.<sup>17</sup> However, an appreciable silane effect was not observed on the thermal and photopolymerization of 4-vinylpyridine, acrylonitrile, styrene, and vinyltrimethoxysilane. We do not currently have the explanation for the unusual silane effect. A detailed study for elucidating it is underway and will be reported in the near future. The cross-linking possibility via hydrosilation of C=O group of poly(MMA) with silyl end groups in the other polymer chains might be slim. The cross-linking process could require high energy, which is anticipated only to occur during the pyrolysis.<sup>18</sup> However, we should admit at this moment that we cannot completely exclude the low degree of cross-linking possibility.

In conclusion, this work describes the thermal and photopolymerization of MMA with phenylsilane. While the polymerization yields and molecular weights of the poly(MMA)s containing phenylsilyl moieties decreased, the TGA residue yields and intensities of SiH stretching IR bands increased as the molar ratio of phenylsilane over MMA increased. The phenylsilyl moiety, once attached to the poly(MMA) as an end group, could be left untouched before the pyrolysis occurring at high temperature. The phenylsilane appeared to competitively and concurrently function as both chain initiation and transfer agents in the polymerization of MMA. The polymerization yield, molecular weight, and TGA residue yield for the thermal polymerization were higher than those for the photopolymerization. A similar silane effect was displayed on the thermal and photopolymerization of methacrylic acid. However, an appreciable silane effect was not observed on the thermal and photopolymerization of 4-vinylpyridine, acrylonitrile, styrene, and vinyltrimethoxysilane.

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