Photopolymerization of Methyl Methacrylate with *p*-X-C₆H₄SiH₃ (X = F, CH₃, OCH₃)

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The bulk photopolymerization of methyl methacrylate (MMA) with *para*-substituted phenylsilanes such as F-C₆H₄SiH₃ (**1**), H₃C-C₆H₄SiH₃ (**2**), and H₃CO-C₆H₄SiH₃ (**3**) was performed to produce poly(MMA)s containing the respective silyl moiety as an end group. 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 over MMA increased. The polymerization yields and polymer molecular weights of MMA with **1-3** increased in the order of **3** < **1** < **2**. These hydrosilanes influence significantly upon the photopolymerization of MMA as both chain-initiation and chain-transfer agents.

Keywords : Photopolymerization, MMA, Phenylsilane.

Introduction

Green and handy light-initiated polymerization technology is widely used for commercial applications in the versatile areas of surface coatings, photoresists, adhesives, and holography.[1] Only a few vinyl monomers including methyl methacrylate (MMA) absorb the most convenient wavelength of light between 250 and 500 nm for common experimental work. In spite of incomplete understanding of the detailed mechanism of photochemically forming the propagating radicals, it seems to involve the transformation of an electonically excited singlet state of the vinyl monomer to a long-lived excited triplet state.[2]

Hydrosilanes are known to undergo many reactions including catalytic hydrosilation of olefins.[3-6] The hydrosilation has been employed to prepare many interesting types of silicon-containing polymers including dendrimers.[7,8] We first reported the bulk photopolymerization of MMA with various hydrosilanes[9] where we demonstrated the easy control of polymerization yield, polymer molecular weight, and thermal stability by adding hydrosilanes into the photopolymerization system. The higher concentration of hydrosilane over MMA produced the shorter chain length of poly(MMA), which, in return, contributed to the increase of thermal stability of poly(MMA). In this paper we report the bulk photopolymerizaion of MMA with 300 nm UV light in the presence of *para*-substituted phenylsilanes such as F-C₆H₄SiH₃ (**1**), H₃C-C₆H₄SiH₃ (**2**), and H₃CO-C₆H₄SiH₃ (**3**) to give poly(MMA)s possessing the respective silyl moiety as an end group to see the possible *para*-substituent effect of the phenylsilanes on the photopolymerization of MMA.

Experimental Section

Materials and Instrumentation. All reactions and manipulations were carried under prepurified nitrogen atmosphere using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Glasswares were flame-dried or oven-dried before use. Infrared spectra were obtained using a Nicolet 520P FT-IR spectrometer. UV-vis electronic spectra were recorded on an IBM 9420 UV-vis spectrophotometer.

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 Ultrastyragel 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), The polymer sample was heated from 25 to 700 ℃ at a rate of 10 ℃/min. TGA residue yield (as a matter of convenience, read at 400 ℃) 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 mn UV lamp; lamp intensity = 6.93×10^8 hv mL^{-1} min^{-1}) was positioned approximately 17 cm from the reaction quartz tubes. MMA was washed twice with aqueous 5% NaOH (to remove inhibitor), washed twice with distilled water, dried over anhydrous MgSO₄, and distilled at reduced pressure before use. The *para*-subsitituted phenylsilanes **1-3** were prepared by reduction of the respective phenyltriethoxysilane with LiAlH₄ in diehtyl ether.[10] λ_{max} for π-π^* transitions of phenyl groups in the UV-vis electronic spectra

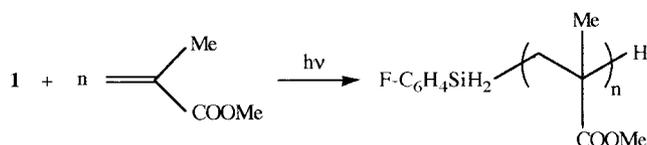(pentane, ε values in parentheses) of **1-3** were shown in 285 nm (3500), 288 nm (3530), and 290 nm (3540), respectively.

Bulk Photopolymerization of MMA with 1-3. Bulk photopolymerization of MMA with different molar ratio of the phenylsilanes (9 : 1 through 3 : 7) was performed. The following procedure is the representative of the photopolymerization reaction. A quartz test tube (1 cm × 10 cm) charged with MMA (1.80 g, 18 mmol) and **1** (0.25 g, 2.0 mmol) was degassed, sealed, and irradiated with UV-light for 6 h.

The polymer was dissolved in toluene, precipitated in hexane, filtered off, and dried to give 1.74 g (85%) of benzene-soluble white solid (TGA residue yield at 400 °C: 12%). The polymer was characterized by ^{1}H NMR, FTIR, GPC, and TGA techniques. FTIR (KBr pellet, cm^{-1}): 2154w (ν_{Si-H}), 1731s ($\nu_{C=O}$). ^{1}H 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$_3$), 4.0-4.3 (m, SiH), 7.2-7.7 (m, ArH). GPC: M_w = 22020. M_n = 14860, M_w/M_n (PDI) = 1.5.

Results and Discussion

Bulk Photopoylmerization of MMA with 1. The poly-(MMA)s possessing the *p*-F-C$_6$H$_4$SiH$_2$ moiety as an end group with weight average molecular weights (M_w) of 6200-22020 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 ratio of **1** (MMA : **1** = 9 : 1 through 3 : 7).

The polymerizaton yields, GPC, IR, and TGA data are summarized in Table 1.

The poly(MMA)s possessing the *p*-H$_3$C-C$_6$H$_4$SiH$_2$ end group with weight average molecular weights (M_w) of 8130-28090 and TGA residue yields of 12-67% were similarly prepared in 30-93% yields by the bulk polymerization of MMA with different molar ratio of **2**. The characterization data of the bulk photopolymerization with **2** are given in Table 2.

Table 1. Photopolymerization of MMA with **1**[a]

Mol ratio (MMA : **1**)	Yield (%)	Mol wt[b]		Relative intensity[c] IR (ν_{SiH})	TGA residue yield (%, at 400 °C)
		M_w	M_n		
10:0	5	8000	6000	0.0	3
9:1	85	22020	14860	1.0	12
7:3	53	14480	10340	2.0	30
5:5	37	11410	7610	3.2	52
3:7	24	6210	4140	4.7	73

[a] UV-irradiation for 6 h. [b] Measured with GPC (*vs* polystyrene) in THF. [c] Relative ratio with respect to the intensity of ν_{SiH} (MMA : **1** = 9 : 1).

Table 2. Photopolymerization of MMA with **2**[a]

Mol ratio (MMA:**2**)	Yield (%)	Mol wt[b]		Relative intensity[c] IR (ν_{SiH})	TGA residue yield (%, at 400 °C)
		M_w	M_n		
9:1	93	28090	18720	1.0	12
7:3	65	17060	10660	1.8	26
5:5	46	12960	9260	2.8	48
3:7	30	8130	5810	4.5	67

[a] UV-irradiation for 6 h. [b] Measured with GPC (*vs* polystyrene) in THF. [c] Relative ratio with respect to the intensity of ν_{SiH} (MMA : **2** = 9 : 1).
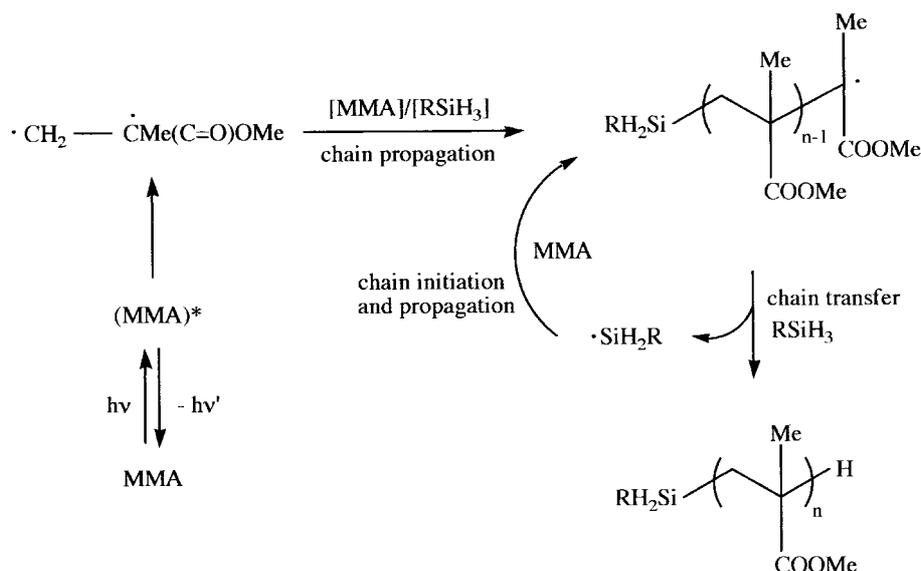
Table 3. Photopolymerization of MMA with **3**[a]

Mol ratio (MMA:**3**)	Yield (%)	Mol wt[b]		Relative intensity[c] IR (ν_{SiH})	TGA residue yield (%, at 400 °C)
		M_w	M_n		
9:1	73	21100	14060	1.0	18
7:3	42	12360	7720	1.5	32
5:5	32	9290	6190	2.5	50
3:7	21	6080	4340	4.0	78

[a] UV-irradiation for 6 h. [b] Measured with GPC (*vs* polystyrene) in THF. [c] Relative ratio with respect to the intensity of ν_{SiH} (MMA : **3** = 9 : 1).

The poly(MMA)s possessing the *p*-H$_3$CO-C$_6$H$_4$SiH$_2$ end group with weight average molecular weights (M_w) of 6080-21100 and TGA residue yields of 18-78% were similarly prepared in 21-73% yields by the bulk polymerization of MMA with different molar ratio of **3**. The characterization data of the bulk photopolymerization with **3** are provided in Table 3.

The weight average molecular weight of polymer formed immediately is known to increase generally with increasing polymerization yield in the radical polymerization of vinyl monomers.[1] As shown in Tables 1-3, the *para*-substituted phenylsilanes similarly exhibited the characteristic trends as the other hydrosilanes did:[9] while the polymer molecular weights and the polymerization yields declined, the relative intensities of Si-H IR stretching bands and the TGA residue yields increased with increasing the silane molar ratio over MMA. The weak resonances corresponding to the expected *para*-substituted phenylsilyl end groups were shown, but the resonances corresponding to the potential vinyl end groups were not observed in the ^{1}H NMR spectra of the poly-(MMA)s within detectable limit. The polymerization yields and polymer molecular weights of MMA with **1-3** increased the order of **3** < **1** < **2**. 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 α-position.[11] The substitution of methyl group decreases the hydrogen donation ability of the silane, but the substitution of phenyl group increases it.[12] One may anticipate that the silane reactivity (which could be directly related to the hydrogen donation ability of the silane) should increase in the order of **1** < **2** < **3** toward the photopolymerization in consideration of only electronic effect because the steric effect of *para*-substituent should be negligible. However, the reactivity order

Scheme 1. Postulated mechanism for photopolymerization of MMA with $RSiH_3$.

of **3** is apparently opposite to the expectation. We have no explanation for this odd reactivity order at this moment. The mechanism for the photopolymerization of MMA with **1-3** could be similar to those with other hydrosilanes (Scheme 1).[9]

λ_{max} for $\pi \rightarrow \pi^*$ transitions of phenyl groups in the UV-vis electronic spectra (pentane, ε values in parentheses) of **1-3** were appeared in 285 nm (3500), 288 nm (3530), and 290 nm (3540), respectively. As shown in Tables 1-3, the presence of hydrosilane in the photopolymerization of MMA is critical because the photopolymerization in the absence of hydrosilanes occurs in a little degree. Both MMA and *p*-substituted phenylsilanes can absorb the light around 300 nm. Nonetheless, it is well documented that the light absorption of MMA molecule produces an excited singlet state of MMA which may then either fluoresce with returning to the ground state of MMA or may be converted to a long-lived triplet excited state, diradical of MMA monomer.[2] 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 keep attacking on the other MMAs to produce poly(MMA)s. At neat condition the latter will be a predominant process to produce poly(MMA) radicals. At high MMA/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 increasing 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 end group.[9] The higher concentration of hydrosilane over MMA produces the shorter chain lenght of poly(MMA), which, in return, contributes to the increase of thermal stability of poly(MMA).

The silane seems to play important roles in the photopolymerization as both chain-initiation and chain-transfer agents by operating competitively and simultaneously. We presume that hydrosilanes could assist the initiation of the polymerization and prevent some unidentified termination reactions from being occurred.

The direct chain transfer constants of the *para*-substituted phenylsilanes for radical polymerization of MMA are not known. Nonetheless, one may expect that they could serve as an excellent chain-transfer agent because $PhSiH_3$ has low Si-H bond energy of 88.2 kcal/mol[13] 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.[14] For example, chain-transfer constant for radical polymerization of MMA at 60 °C is reported to be 2.7 for thiophenol and 0.12 for triphenylsilane.[15]

In summary, this work describes the photopolymerization of MMA with *para*-substituted phenylsilanes **1-3**. For these silanes, while the polymerization yields and the molecular weights of the poly(MMA)s possessing the respective silyl end group decreased, the TGA residue yields and the intensities of Si-H stretching IR bonds increased as the molar ratio of silane over MMA increased. The polymerization yields and polymer molecular weights of MMA with **1-3** increased in the order of **3** < **1** < **2**. The hydrosilyl moieties, once attached to the poly(MMA)s as end group, could be left untouched at mild temperature before the pyrolysis occurring at high temperature. We showed the easy control of polymerization yield, polymer molecular weight, and thermal stability by adding hydrosilanes into the photopolymerization system. The silanes appear to competitively and concurrently act as both chain-initiation and chain-transfer agents in the photopolymerization of MMA.

References

1. (a) Odian, G. *Principles of Polymerization,* 3rd ed.; Wiley: New York, 1991; pp 222-223. (b) Mimura, S.; Naito, H.;

Kanemitsu, Y.; Matsukawa, K.; Inoue, H. *J. Organomet. Chem.* **2000**, *611*, 40. (c) Peinado, C.; Alonso, A.; Catalina, F.; Schnabel, W. *J. Photochem, & Photobiol. A: Chemistry* **2001**, *141*, 85.

2. Norrish, R. G.; Simons, J. P. *Proc. Roy. Soc. (London)* **1959**, *A251*, 4.

3. Chatgilialoglu, C.; Ferreri, C.; Lucarini, M.; Pedrielli, P.; Pedulli, G. F. *Organometallics* **1995**, *14*, 2672.

4. Corriu, R. J. P. *J. Organomet. Chem.* **1990**, *400*, 81.

5. (a) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *J. Am. Chem. Soc.* **1992**, *114*, 7047. (b) Woo, H.-G.; Kim, S.-Y.; Han, M.-K.; Cho, E. J.; Jung, I. N. *Organometallics* **1995**, *14*, 2415. (c) Gauvin, F.; Harrod, J. F.; Woo, H.-G. *Adv. Organomet. Chem.* **1998**, *42*, 363. (d) Shu, R.; Hao, L.; Harrod, J. F.; Woo, H.-G.; Samuel, E. *J. Am. Chem. Soc.* **1998**, *120*, 12988.

6. Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 2, pp 115-120.

7. (a) Carothers, T. W.; Mathias, L. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*(1), 503. (b) Seyferth, D.; Son, D. Y.; Rheingold, A. L.; Ostrander, R. L. *Organometallics* **1994**, *13*, 2682. (c) Mathias, L. J.; Carothers, T. W. *J. Am. Chem. Soc.* **1991**, *113*, 4043.

8. (a) Sun, F.; Grainger, D. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*(1), 137. (b) Lewis, C. M.; Mathias, L. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34*(1), 491. (c) Greber, G.; Hallensleben, M. L. *Makromol. Chem.* **1965**, *83*, 148. (d) Boury, B.; Corriu, R. J. P.; Leclercq, D.; Mutin, P. H.; Planeix, J. M.; Vioux, A. *Organometallics* **1991**, *10*, 1457.

9. (a) Hong, L.-Y.; Woo, H.-G.; Ham, H. S. *Bull. Korean Chem. Soc.* **1995**, *16*, 360. (b) Woo, H.-G.; Hong, L.-Y.; Kim, S.-Y.; Park, S.-H.; Song, S.-J.; Ham, H.-S. *Bull. Korean Chem. Soc.* **1995**, *16*, 774. (c) Woo, H.-G.; Hong, L.-Y.; Park, J.-Y.; Jeong, Y.-T.; Park, H. R.; Ham, H.-S. *Bull. Korean Chem. Soc.* **1996**, *17*, 16. (d) Woo, H.-G.; Oh, E.-M.; Park, J.-H.; Kim, B.-H.; Kim, Y.-N.; Yoon, C.-H.; Ham, H.-S. *Bull. Korean Chem. Soc.* **2000**, *21*, 291.

10. (a) Woo, H.-G. *Ph. D. Thesis*; University of California at San Diego: 1990. (b) Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Macromolecules* **1991**, *24*, 6863. (c) Imori, T.; Woo, H.-G.; Walzer, J. F.; Tilley, T. D. *Chem. Mater.* **1993**, *5*, 1487 and references theirin.

11. Kanabus-Kaminska, J. M.; Hawari, J. A.; Griller, D. *J. Am Chem. Soc.* **1987**, *109*, 5268.

12. Ballestri, M.; Chatgilialoglu, C.; Guerra, M.; Guerrini. A.; Lucarini, M.; Seconi, G. *J. Chem. Soc., Perkin Trans. 2.* **1993**, 421 and references therin.

13. Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.

14. Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins College Publishers: New York, 1993; p A25.

15. Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; Wiely: New York, 1989.