Photopolymerization of Methyl Methacrylate with 1,4-C₆H₄(SiH₃₋ₓMeₓ)₂

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The bulk photopolymerization of methyl methacrylate (MMA) with bis(silane)s such as 1,4-C₆H₄(SiH₃)₂ (**1**) and 1,4-C₆H₄(SiH₂Me)₂ (**2**) was performed to produce poly(MMA)s possessing the corresponding bis(silyl) moiety as an end group. For the bis(silane)s, while the polymerization yields and the polymer molecular weights decreased, the TGA residue yields and the relative intensities of Si-H IR stretching bands increased as the relative bis(silane) concentration over MMA increased. The polymerization yield, polymer molecular weight, and TGA residue yield of MMA with **1** were found to be higher than those with **2**. The bis(silane)s appears to influence significantly upon the photopolymerization of MMA as both chain initiation and chain transfer agents.

Introduction

Convenient and clean photopolymerization technology is extensively used for commercial applications in the versatile areas of surface coatings, photoresists, adhesives, and holography.[1] Only a few unsaturated monomers including methyl methacrylate (MMA) are known to absorb light between 250 and 500 nm which is the most convenient wavelength range for common experimental work. Although the detailed mechanism of photochemically forming the propagating radicals is not throughly 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 undergo many intriguing reactions such as free radical reduction of organic halides,[3] nucleophilic reduction of carbonyl compounds,[4] dehydrogenative Si-Si coupling,[5] and hydrosilation of olefins with catalyst.[6] The hydrosilation has been used to prepare many interesting types of silicon-containing polymers such as dendrimers[7] and copolymers.[8] We reported the bulk photopolymerization of MMA with various hydrosilanes.[9] In this paper we report the bulk photopolymerization of MMA with 300-nm UV light in the presence of bis(silane)s 1,4-C₆H₄(SiH₃)₂ (**1**) and 1,4-C₆H₄-(SiH₂Me)₂ (**2**) to give poly(MMA)s containing the bis(silyl) moiety as an end group.

Experimental Section

Materials and Instrumentation. All reactions and manipulations were performed under prepurified nitrogen atmosphere using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. Glassware was flame-dried or oven-dried before use. Approximate distances between silicon atoms of hydrosilanes with two silyl groups were obtained by using CS Chem 3D Pro™ program (version 3.0) developed by the Cambridge Soft Corporation operating on a Power Macintosh personal computer. 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 Ultrastyragel GPC column series (sequence 10³, 10⁴, 10⁵, 10⁶ 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× 10¹⁸ hv mL⁻¹min⁻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 bis(ethoxysilane)s 1,4-C₆H₄[Si(OEt)₃]₂ and 1,4-C₆H₄[Si(OEt)₂Me]₂ were obtained by the reaction of 1,4-C₆H₄(MgBr)₂ with Si(OEt)₄ and MeSi(OEt)₃, respectively, in THF. The bis(silane)s **1** and **2** were prepared by reduction of the bis(ethoxysilane)s with LiAlH₄ in diethyl ether.[10]
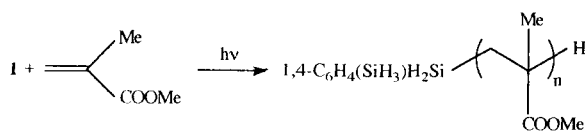
Bulk Photopolymerization of MMA with Bis(silane)s. Bulk photopolymerization of MMA with different molar ratio of bis(silane) (18 : 1 through 3 : 7) was carried out. The following procedure is representative of the photopolymerization reactions. A quartz test tube (1 cm× 10 cm) charged with MMA (1.80 g, 18 mmol) and **1** (0.28 g, 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 1.93 g (93%) of benzene-soluble white solid (TGA residue yield at 400°C: 8%). The polymer was characterized by ^{1}H MNR, IR, GPC, and TGA techniques. IR (KBr pellet, cm^{-1}): 2162 w (v_{Si-H}) 1743 s ($v_{C=O}$). ^{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=12800, M_n=9300, M_w/M_n (PDI)= 1.4.

Results and Discussion

Bulk Photopolymerization of MMA with 1. The poly-(MMA)s possessing the bis(silyl) moiety with weight average molecular weights (M_w) of 7000-13900 and TGA residue yields of 6-32% were prepared in 20-93% yields by 300 nm UV light-initiated bulk polymerization of MMA with different molar ratio of 1 (MMA : 1=18 : 1 through 3 : 7).

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

Bulk Photopolymerization of MMA with 2. The Poly-(MMA)s containing the bis(methylsilyl) moiety with M_w of 7600-10100 and TGA residue yields of 2-30% were prepared in 18-75% yields by 300 nm UV light-initiated bulk polymerization of MMA with different molar ratio of 2 (MMA : 2=18 : 1 through 3 : 7). The characterization data of the bulk photopolymerization with 2 are given in Table 2.

The weight average molecular weight of polymer formed immediately is known to increase generally with augment of polymerization yield in the radical polymerization of vinyl monomers.[1] As shown in Tables 1 and 2, the bis(silane)s 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 augmented with increasing the bis(silane) molar ratio over MMA. The resonances corresponding to the expected bis(silyl) end

Table 1. Photopolymerization of MMA with 1,4-C$_6$H$_4$- (SiH$_3$)$_2$[a]

Mol ratio (MMA:Silane)	Yield (%)	Mol wt[b]		Relative intensity[c] IR (v_{Si-H})	TGA residue yield (%, at 400 °C)
		M_w	M_n		
18:0	5	8000	6000	0	3
18:1	89	13900	11000	1.0	6
9:1	93	12800	9300	2.0	8
7:3	61	8900	6300	3.0	17
5:5	33	8600	8600	3.8	21
3:7	20	7000	5000	6.0	32

[a]UV-irradiation for 6 h. [b]Measured with GPC (vs polystyrene) in THF. [c]Relative ratio with respect to the intensity of v_{Si-H} (MMA : Silane= 18 : 1).

Table 2. Photopolymerization of MMA with 1,4-C$_6$H$_4$(SiH$_2$Me)$_2$[a]

Mol ratio (MMA:Silane)	Yield (%)	Mol wt[b]		Relative intensity[c] IR (v_{Si-H})	TGA residue yield (%, at 400 °C)
		M_w	M_n		
18:0	71	10500	8500	1.0	2
9:1	75	10100	8600	1.3	5
7:3	49	8300	6600	3.0	10
5:5	25	8100	6000	3.6	19
3:7	18	7600	5000	7.6	30

[a]UV-irradiation for 6 h. [b]Measured with GPC (vs polystyrene) in THF. [c]Relative ratio with respect to the intensity of v_{Si-H} (MMA : Silane= 18 : 1).

groups were shown, but the resonances coresponding to the potential vinyl end groups were not observed in the ^{1}H NMR spectra of the poly(MMA)s even in the molar ratio of 18 : 1 within detectable limit. The polymerization yield, polymer molecular weight, and TGA residue yield of MMA with 1 were found to be higher than those with 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 the 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 expect that 1 should have higher reactivity toward the photopolymerization than 2 in considerations of electronic and steric effects. Above experimental facts can be rationalized as follows (*vide infra*). The absorption of light 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. 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.[2] At neat condition the latter will be a predominant process to produce poly(MMA) radicals. At high MMA/low bis(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 bis(silane) concentration. The chain transfer might produce a bis(silyl)radical which, in turn, leads to chain initiation, resulting in the production of poly(MMA) containing the bis(silyl) moiety presumably as an end group as shown in Scheme 1.

The bis(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 bis(silane)s for radical polymerization of MMA are not known. However, we 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/
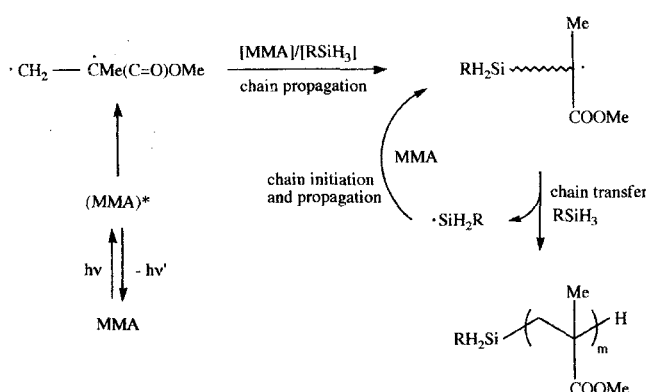
Scheme 2

mol.[14] 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 this study we used two bis(silane)s **1** and **2** to check if they may function as a cross-linking agent in the photopolymerization of MMA because various hydrosilanes such as $RSiH_3$, R_2SiH_2, $(PhSiH_2)_2$, and $PhCH(SiH_3)_2$ appear to be not a candidate of cross-linking agent.[9] While the Si-Si distance (obtained by using CS Chem 3D Pro^{TM} program) of $(PhSiH_2)_2$, and $PhCH(SiH_3)_2$ are 2.22 and 3.07 Å, respectively, that of **1** and **2** is appoximately 6.43 Å. Transition-metal group 4 metallocene-catalyzed Si-Si dehydroocupling of **1**, **2**, and $PhCH(SiH_3)_2$ is reported to produce an extensive network structure of insoluble polysilane, whereas the catalytic Si-Si dehydrocoupling of $(PhSiH_2)_2$ produces a soluble polysilane.[10,16,17] We anticipated that **1** and **2** might be a good cross-linking agent because the bis(silane)s have a long distance between two silyl groups and a low Si-H bond energy due to the silyl substituent. However, the hydrogen donation ability of a hydrosilane for cross-linking poly(MMA) chains appears to be not related always to the Si-H bond energy of a hydrosilane. In view of the following facts: (1) the trend of solubility, polymerization yields, and molecular weight distributions with varying 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 *via* hydrosilation of C=O group of poly(MMA) with silyl end groups in the other polymer chains might be very low. The cross-linking process could require high energy, which is anticipated only to occur during the pyrolysis at high temperature.[18] Nevertheless, we should confess at this moment that we cannot exclude the cross-linking possibility completely.

In summary, this work describes the photopolymerization of MMA with bis(silane)s **1** and **2**. The polymerization yields and the molecular weights of the poly(MMA)s possessing bis(silyl) moieties decreased, whereas the TGA residue yields and the intensities of Si-H stretching IR bands increased as the molar ratio of bis(silane) over MMA increased. The polymerization yield, polymer molecular weight, and TGA residue yield of MMA with **1** were higher than those with **2** probably due to its steric and electronic effects. The bis(silyl) moieties, once attached to the poly(MMA)s as end group,

could be left untouched and uncross-linked before the pyrolysis occurring at high temperature. The silanes appeared to competitively and concurrently function as both chain initiation and transfer agents in the photopolymerization of MMA. A plausible mechanism for the photopolymerization of MMA was provided.

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