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Photopolymerization of Methyl Methacrylate with Primary Aryl- and Alkylsilanes

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The bulk photopolymerization of methyl methacrylate (MMA) with primary arylsilane (e.g., phenylsilane) and various primary alkylsilanes (e.g., benzylsilane, 3-phenoxyphenyl-1-silabutane, 3-naphthyl-1-silabutane, and 3-chlorophenyl-1-silabutane) was performed to produce poly(MMA)s containing the corresponding silyl moiety as an end group. It was found for the phenylsilane that while the polymerization yields increased and then decreased with a turning point at the molar ratio of MMA : silane = 10 : 1 as the relative silane concentration increases, the polymer molecular weights decreased, and the TGA residue yields and the relative intensities of SiH IR stretching bands increased with increment of molar ratio of silane over MMA. The photopolymerization yield of MMA with the arylsilane was found to be higher than those with the alkylsilanes and without the silanes. Thus, the silanes seemed to significantly influence on the photopolymerization as both chain initiation and chain transfer agents.

Introduction

A great amount of attention has been paid to photopolymerization of vinyl monomers because of its distinct advantages such as convenience and the avoidance of chemical contamination by initiator residues. Photopolymerization technology is employed on a commercial scale today in the

areas of surface coatings, photoresists, adhesives, and holography.¹ Any vinyl monomer that will undergo chain reaction polymerization is subject to photopolymerization or photosensitized polymerization, but 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. Methyl methacrylate is susceptible to direct

photopolymerization on the exposure to 300-nm wavelength light. Although 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

Hydrosilane is known to undergo many interesting reactions such as free radical reduction of organic halides,^{3a,b} nucleophilic reduction of carbonyl compounds,^{3c} dehydrogenative Si-Si coupling,⁴ and hydrosilation of olefins with catalyst.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 used to prepare many interesting types of silicon containing polymers such as dendrimers⁶ and copolymers.⁷ Various rigid poly(MMA) products, such as sheet, rod, and tube, are produced by bulk polymerization in a casting process. In the present paper we report the bulk photopolymerization of MMA with 300-nm UV light in the presence of various primary aryl- and alkylsilanes to give versatile poly(MMA)s containing the corresponding silyl moiety as an end group.

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 $CDCl_3/CHCl_3$ 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 Ultrastaygel 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 °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 = 6.93×10^{18} hv mL⁻¹ min⁻¹) was positioned approximately 17 cm from the reaction quartz tube. MMA was washed twice with aqueous 5% NaOH (to remove inhibitor), washed twice with distilled water, dried over $MgSO_4$, and distilled at reduced pressure before use. 3-Phenoxyphenyl-1-silabutane, 3-naphthyl-1-silabutane, and 3-chlorophenyl-1-silabutane⁸ were kindly provided by Dr. Il Nam Jung of the Korea Institute of Science and Technology. $PhCH_2SiH_3$ and $PhSiH_3$ were prepared by reduction of

Table 1. GPC Characterization of Photopolymerization of MMA with Phenylsilane^a

Mol ratio (MMA : Silane)	Yield (%)	Mol wt ^b	
		M_w	M_n
10:0	5	8000	6000
10:0.1	24	539000	222000
10:0.3	27	189000	105000
10:0.5	30	185000	90000
10:0.7	45	152000	71000
10:1.0	92	53000	35000
10:4.3	44	22000	14000
10:10	25	12000	8000
10:23	7	11000	9000

^aUV-irradiation for 6 h. ^bMeasured with GPC in THF.

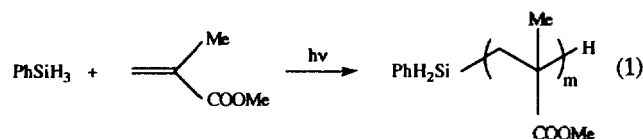
$PhCH_2SiCl_3$ and $PhSiCl_3$ (Hüls America Inc.), respectively, with $LiAlH_4$ in diethyl ether.⁹

Bulk Photopolymerization of MMA with Primary Aryl- and Alkylsilanes. Bulk photopolymerization of MMA with various alkylsilanes (molar ratio of 10 : 1) was performed. Bulk photopolymerization of MMA with different molar ratio of $PhSiH_3$ (10 : 0.1 through 10 : 23) was also 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 2.03 g (92%) of benzene-soluble white solid (TGA residue yield at 400 °C : 17%). The polymer was characterized by ¹H NMR, IR, GPC, and TGA techniques. IR (KBr pellet, cm⁻¹): 2170 w (ν_{Si-H}), 1728 s ($\nu_{C=O}$). ¹H NMR (δ , $CDCl_3$, 300 MHz): 0.7-1.1 (m, 3H, C-CH₃), 1.7-2.1 (m, 2H, CH₂), 3.6 (m, 3H, OCH₃), 4.0-4.3 (m, SiH), 5.6, 6.1 (br, H₂C=), 7.2-7.7 (m, ArH). GPC: $M_w = 53000$, $M_n = 35000$, M_w/M_n (PDI) = 1.5.

Results and Discussion

Bulk Photopolymerization of MMA with Arylsilane.

The poly(MMA)s containing phenylsilyl moiety with weight average molecular weights of 11000-539000 and TGA residue yields of 10-39% were prepared in 7-92% yields by 300 nm UV light-initiated bulk polymerization of MMA with different molar ratio of phenylsilane (MMA : phenylsilane = 10 : 0.1 through 10 : 23) (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.

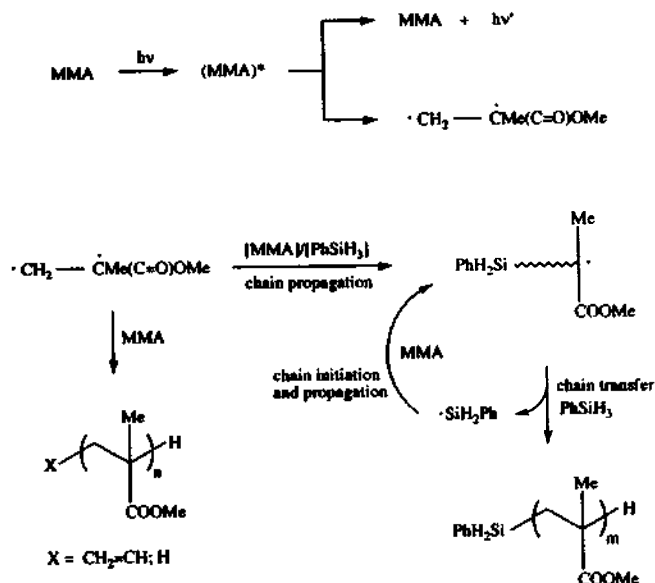
It is well known that high-molecular-weight polymer is formed immediately and that the weight average molecular weight generally increases with increase of polymerization

Table 2. Photopolymerization of MMA with Phenylsilane^a

Mol ratio (MMA : Silane)	Relative intensity ^b IR (ν_{SiH})	TGA residue yield (%, at 400 °C)
10:0	0	3
10:0.1	1.0	10
10:0.3	1.5	12
10:0.5	1.8	14
10:0.7	2.3	15
10:1.0	2.5	17
10:4.3	3.0	22
10:10	4.2	31
10:23	5.0	39

^aUV-irradiation for 6 h. ^bRelative ratio with respect to the intensity of ν_{SiH} (MMA : Silane = 10 : 0.1).

yield in the radical polymerization of vinyl monomers.¹ At any instant the reaction mixture contains only monomer, high polymer, and the growing chains; *i.e.*, the molecular weight of the polymer is relatively unchanged during the polymerization, although the polymerization yield increases with reaction time. As shown in Table 1 and 2, the polymerization yields increased, reached to the highest yield in the molar ratio of 10 : 1 and then decreased with increasing the silane molar ratio over MMA. While the polymer molecular weights declined, the relative intensities of SiH IR stretching bands and TGA residue yields augmented as the molar ratio of silane over MMA increased. It should be also noted that the molecular weight of the polymer and polymerization yield with silane for the photopolymerization of molar ratio of MMA : silane = 10 : 1 were much higher than without silane. In other words, the silane appears to help the photopolymerization of MMA until the molar ratio of MMA : silane reaches at 10, but to hamper the reaction after the molar ratio with increase of the silane concentration. The resonances corresponding to the vinyl end groups were clearly shown in the ¹H NMR spectrum of the poly(MMA) in the molar ratio of 10 : 0.1. The intensity of the vinyl resonances gradually weaken with increasing the molar ratio of silane over MMA, and ended up being completely disappeared. We believe the polymers produced in the molar ratio range of 10 : 0.1-1.0 might be a mixture of two kinds of polymers with a vinyl end group or with a silyl end group. A study for verifying the matter is in progress using GPC and DSC analysis techniques. These facts 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 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

**Scheme 1.** Postulated Mechanism for Photoreaction of MMA with Phenylsilane.**Table 3.** Photopolymerization Yields of MMA with Various Silanes^a

Silane	Yield (%)
benzylsilane	2
3-phenoxyphenyl-1-silabutane	1
3-naphthyl-1-silabutane	4
3-chlorophenyl-1-silabutane	19
phenylsilane	92

^aUV-irradiation for 6 h; Molar ratio of MMA : silane = 10 : 1.

initiation, resulting in the production of poly(MMA) containing the silyl moiety as an end group as shown in Scheme 1.

The silane seems to affect on the photopolymerization as both chain initiation and chain transfer agents by operating competitively and simultaneously. Although the direct chain transfer constants of the arylsilanes for radical polymerization of MMA are not available, they could serve as an excellent chain transfer agent because PhSiH₃ has low Si-H bond energy of 88.2 kcal/mol¹⁰ which is comparable to S-H bond energy of mercaptans, known to data to be one of most powerful chain transfer agents, of 87 kcal/mol.¹¹ 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

Bulk Photopolymerization of MMA with Alkylsilane. The poly(MMA)s containing corresponding alkylsilyl moiety were prepared in 2-19% yields by 300 nm UV light-initiated bulk polymerization of MMA with fixed molar ratio of alkylsilane (MMA : silane = 10 : 1).

In the present study we employed aryl substituted alkylsilane, 3-aryl-1-silabutanes because we wanted to check the effect of aryl group on the photopolymerization. The effect of the aryl group turned out to be negligible as shown in

Table 3. Photopolymerization of MMA with aryl group-free alkylsilanes produced the corresponding poly(MMA)s in very low yields.¹³ 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 α -position.^{3a} It is recently reported that the substitution of methyl group decreases the hydrogen donation ability of the silane, but the substitution of phenyl group increases it.¹⁴ The hydrogen donation ability of a silane appears to be not related always to the Si-H bond energy of a silane. In consideration of the following items: (1) the trend of solubility, polymerization yields, and molecular weight distributions with variation of 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 slim. The cross-linking process could require high energy, which is anticipated only to occur during the pyrolysis.¹⁵ However, we should admit at this moment that we cannot exclude the cross-linking possibility completely. Interestingly, the polymerization yield of MMA with 3-chlorophenyl-1-silabutane was higher than with other similar series of silanes such as 3-phenoxyphenyl-1-silabutane and 3-naphthyl-1-silabutane. We believe that in the photopolymerization of MMA with the chlorophenyl-1-silabutane, the photochemical cleavage could occur predominantly at the site of the C-Cl bond.¹⁶

In conclusion, this work describes the photopolymerization of MMA with arylsilane and alkylsilane. While the polymerization yields and molecular weights of the poly(MMA)s containing silyl moieties decreased, the TGA residue yields and intensities of SiH stretching IR bands increased as the molar ratio of silane over MMA increased. The photopolymerization yield of MMA with the arylsilane was found to be higher than those with the alkylsilanes and without the silanes. The silyl moieties, once attached to the poly(MMA) as end group, could be left untouched 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 was proposed.

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