

Photopolymerization of Methacrylic Acid with Secondary Silanes

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Received March 16, 1996

The bulk photopolymerization of methacrylic acid (MA) with secondary silanes such as PhMeSiH_2 and Ph_2SiH_2 gave poly(MA)s possessing the secondary silyl moiety presumably as an end group. It was found that while the polymerization yields and intrinsic viscosities decreased, the TGA residue yields and the relative intensities of SiH IR stretching bands increased with increasing mole ratio of the secondary silane over MA. The sterically less bulky silane PhMeSiH_2 produced poly(MA)s with somewhat higher molecular weights and with similar TGA residue yields, compared with the sterically bulkier silane Ph_2SiH_2 . The secondary silanes seem to significantly influence on the photopolymerization of MA as both chain initiation and chain transfer agents.

Introduction

Photopolymerization technology applicable conveniently is commercially and amply used today in the areas of surface coatings, photoresists, adhesives, and holography. A wide variety of unsaturated vinyl derivatives can be polymerized *via* a free-radical chain process.¹ Albeit any vinyl derivative that will undergo chain polymerization is, in principle, subject to photopolymerization or photosensitized polymerization, only a few unsaturated compounds are known to absorb 250–500 nm wavelength light which is the most convenient wavelength range for experimental work. The detailed mechanism forming the propagating radicals is not completely understood, but it appears to involve the conversion of an electronically excited singlet state of the monomer to a long-lived excited triplet state.² The capability performing a thermodynamically possible polymerization counts upon its kinetic feasibility on whether the process proceeds at a reasonable rate under a provided set of reaction conditions. Hence, an initiator (or promotor) is often needed to attain the kinetic feasibility.

Hydrosilanes have taken part in versatile catalytic reactions such as free radical reduction of organic halides,³ nucleophilic reduction of carbonyl compounds,⁴ dehydropolymerization,⁵ cross-dehydrocoupling,⁶ and hydrosilation of olefins.⁷ The hydrosilation has been applied to prepare many interesting types of silicon containing polymers such as dendrimers⁸ and copolymers.⁹ We reported the bulk photopolymerization of methyl methacrylate (MMA) with various silanes to produce poly(methyl methacrylates), poly(MMA)s containing the corresponding silyl moiety probably as an end group.¹⁰ We recently described the bulk photopolymerization of methacrylic acid (MA) with primary silane.¹¹ In the present paper we wish to report the bulk photopolymerization of MA with secondary silanes giving poly(methacrylic acids), poly(MA)s containing the silyl moiety presumably as an end group in order to compare the silane effect on the photopolymerization of MA.

Experimental Section

Materials and Instrumentation. All reactions and

manipulations were performed under prepurified nitrogen using Schlenk techniques. Dry, oxygen-free solvents were used 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 $\text{DMSO-}d_6/\text{DMSO-}H_6$ as a reference at 2.49 ppm downfield from TMS. Reduced viscosity (η_{red}) and inherent viscosity (η_{inh}) of different concentration (c in g/dL) of polymer solutions in DMF were obtained by measuring three satisfactory readings of the efflux time (polymer, t ; solvent, t_s) with an Ostwald-Fenske viscometer immersed in the constant-temperature bath maintaining at 25 ± 0.01 °C and by substituting the mean of three readings into the known equations.¹² The extrapolation of the two viscosities to the same intercept as c approached to zero afforded the intrinsic viscosity $[\eta]$ in dL/g. 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 (for convenience sake, 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. Methacrylic acid (Aldrich Chemical Co.) was saturated with NaCl (to remove the bulk of the water), then the organic phase was dried with CaCl_2 and distilled under vacuum before use. PhMeSiH_2 and Ph_2SiH_2 were prepared by reduction of PhMeSiCl_2 and Ph_2SiCl_2 (Aldrich Chemical Co.), respectively, with LiAlH_4 (Aldrich Chemical Co.) in diethyl ether.¹³

Bulk Photopolymerization of MA with Phenylmethylsilane. Bulk photopolymerization of MA with different mole ratio of PhMeSiH_2 (10 : 1 through 3 : 7) was performed. In a typical experiment, a quartz test tube (1 cm × 20 cm) charged with MA (1.72 g, 20 mmol) and PhMeSiH_2 (0.24 g, 2.0 mmol) was degassed, sealed, and irradiated with 300

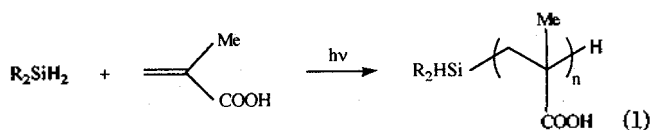
nm UV-light for 6 h. The polymer was taken in methanol, precipitated in diethyl ether, filtered off, and dried to give 1.67 g (85%) of white solid (TGA residue yield at 400 °C: 62%). ¹H NMR (δ, DMSO-d₆, 300 MHz): 0.35 (m, Si-CH₃), 0.9-1.1 (br, 3H, C-CH₃), 1.8-2.1 (br, 2H, CH₂), 7.2-7.7 (m, ArH), 12.3 (br, 1H, OH). The SiH resonance was not clearly observed in the ¹H NMR spectrum for uncertain reasons. IR (KBr pellet, cm⁻¹): 3400 br s (ν_{O-H}), 2168 w (ν_{Si-H}), 1715 s (ν_{C=O}). Intrinsic viscosity: 0.62 dL/g.

Bulk Photopolymerization of MA with Diphenylsilane. Bulk photopolymerization of MA with different mole ratio of Ph₂SiH₂ (10 : 1 through 3 : 7) was carried out. The following procedure is representative of the polymerization reactions. A quartz test tube (1 cm × 20 cm) was loaded with MA (1.72 g, 20 mmol) and Ph₂SiH₂ (0.37 g, 2.0 mmol). The mixture was degassed, sealed, and UV-irradiated for 6 h. The polymer was dissolved in methanol, precipitated in diethyl ether, filtered off, and dried to give 1.94 g (93%) of white solid (TGA residue yield at 400 °C: 60%). ¹H NMR (δ, DMSO-d₆, 300 MHz): 0.9-1.1 (br, 3H, C-CH₃), 1.8-2.1 (br, 2H, CH₂), 7.3-7.7 (m, ArH), 12.3 (br, 1H, OH). The SiH resonance was not clearly observed in the ¹H NMR spectrum. IR (KBr pellet, cm⁻¹): 3400 br s (ν_{O-H}), 2140 w (ν_{Si-H}), 1704 s (ν_{C=O}). Intrinsic viscosity: 0.38 dL/g.

Results and Discussion

The poly(MA)s containing phenylmethylsilyl moiety with intrinsic viscosities of 0.17-0.62 dL/g and TGA residue yields of 62-69% were prepared in 14-85% yields by bulk photopolymerization of MA with different mole ratio of phenylmethylsilane (MA : phenylmethylsilane = 10 : 1 through 3 : 7). The polymers were soluble in DMF, DMSO, and methanol. The characterization data of the resulting poly(MA)s are summarized in Table 1.

The poly(MA)s containing diphenylsilyl moiety with intrinsic viscosities of 0.19-0.38 dL/g and TGA residue yields of 60-68% were also synthesized in 8-93% yields by bulk photopolymerization of MA with different mole ratio of diphenylsilane (MA : diphenylsilane = 10 : 1 through 3 : 7) (eq. 1).



The polymers were soluble in DMF, DMSO, and methanol. The characterization data of the resulting poly(MA)s are listed in Table 2.

It is known that high-molecular-weight polymer is formed instantly and that the weight average molecular weight generally increases with increase of polymerization yield in the radical polymerization of vinyl monomers.¹ The intrinsic viscosity is directly related to the weight average molecular weight of polymer.¹² As shown in Table 1 and Table 2, while the polymerization yields and intrinsic viscosities [η] decreased, the relative intensities of SiH IR stretching bands and TGA residue yields increased as the mole ratio of silane over MA augmented. These facts can be rationalized as follows (*vide infra*). The absorption of light may produce an

Table 1. Characterization of Photopolymerization of MA with Phenylmethylsilane^a

Mol ratio (MA:Silane)	Yield (%)	Intrinsic viscosity ^b [η]	Relative intensity ^c IR (ν _{SiH})	TGA residue yield (% at 400 °C)
10:1	85	0.62	1.0	62
7:3	43	0.36	1.9	67
5:5	31	0.27	2.7	68
3:7	14	0.17	3.2	69

^aUV-irradiation for 6 h. ^bMeasured in DMF at 25 °C; unit, dL/g.

^cRelative ratio with respect to the intensity of ν_{SiH} (MA : phenylmethylsilane = 10 : 1).

Table 2. Characterization of Photopolymerization of MA with Diphenylsilane^a

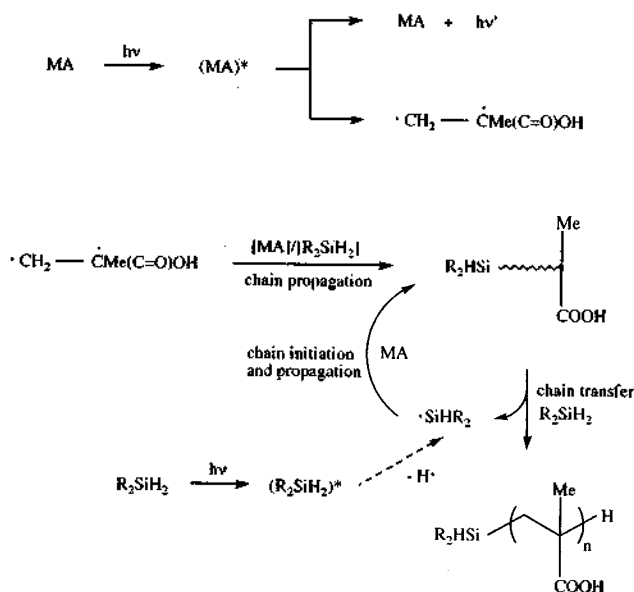
Mol ratio (MA:Silane)	Yield (%)	Intrinsic viscosity ^b [η]	Relative intensity ^c IR (ν _{SiH})	TGA residue yield (% at 400 °C)
10:1	93	0.38	1.0	60
7:3	47	0.24	1.8	66
5:5	31	0.21	2.7	67
3:7	8	0.19	3.2	68

^aUV-irradiation for 6 h. ^bMeasured in DMF at 25 °C; unit, dL/g.

^cRelative ratio with respect to the intensity of ν_{SiH} (MA : diphenylsilane = 10 : 1).

excited singlet state of MA which will either fluoresce or be converted to an excited and long-lived triplet excited state, diradical of MA monomer. Attack on the other MA by this diradical affords a new diradical of MA dimer which either reverts to the ground state two MA molecules or attacks on the other MA that ultimately initiate polymerization.² At neat condition the latter will be a predominant process to produce poly(MA) radicals. At high MA or low silane concentrations, chain propagation will be able to compete with chain transfer over the poly(MA) radicals. However, the chain transfer will eventually rule over the 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(MA) containing the silyl moiety as an end group as shown in Scheme 1.

It is known that polysilyl radicals generated from the photochemical homolysis of polysilanes may initiate the free-radical chain polymerization of some vinyl monomers.¹⁴ The secondary silanes seem to considerably affect on the photopolymerization as both chain initiation and chain transfer agents by operating competitively and simultaneously. The direct chain transfer constants of the secondary silanes for radical polymerization of MA are not available. Nonetheless, it could serve as an excellent chain transfer agent because PhSiH₃ has low Si-H bond energy of 88.2 kcal/mol¹⁵ 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.¹⁶ In fact, it has been reported that chain transfer constant for radical polymerization of MMA at 60 °C



Scheme 1. Postulated Mechanism for Photoreaction of MA with Secondary Silane.

is 2.7 for thiophenol and 0.12 for triphenylsilane.¹⁷ 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.³ It is recently reported that the substitution of methyl group on a silane decreases the hydrogen donation ability of the silane, but the substitution of phenyl group increases it.¹⁸ 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 of an arylsilane first absorbs the energy and then transfers it into the silicon center, which leads to the photochemical 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.

As shown in Table 1 and Table 2, the sterically less bulky silane PhMeSiH₂ afforded poly(MA)s with somewhat higher molecular weights than the sterically bulkier silane Ph₂SiH₂. The MA photopolymerization yields were higher than the MMA photopolymerization yields with the secondary silanes.^{10a} The polymerizability of MA by the silyl radical seems to be naturally higher than that of MMA. The TGA residue yields of poly(MA)s with the secondary silanes were much higher than those of poly(MMA)s with the secondary silanes.¹⁰ The change of the TGA residue yields of the poly(MA)s with increasing the relative silane concentration was very little when compared to that of the poly(MMA)s. It is interesting to note that while the weight loss of the poly(MMA)s was smoothly occurred up to 350 °C with few turning points, the abrupt weight loss of a narrow range of the poly(MA)s was occurred twice at the turning points around 150 °C and 250 °C before 350 °C (Figure 1), although all the poly(MA)s and poly(MMA)s rapidly and exhaustively decomposed after 350 °C.

We believe that cross-linking reactions could be happened by the acidolysis between Si-H group and acid group in the different polymer chains at around 150 °C, yielding a silyl

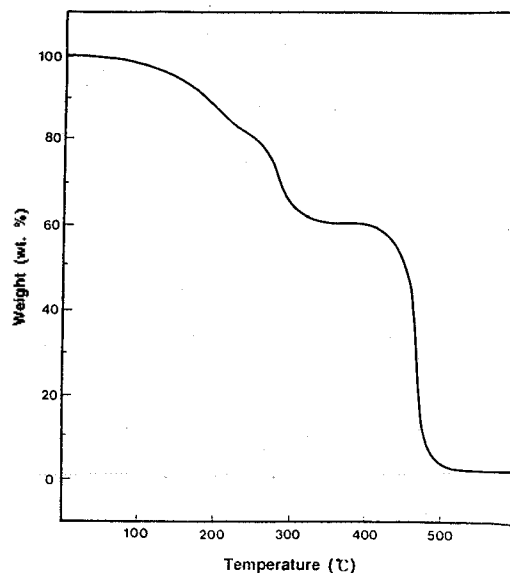


Figure 1. TGA thermogram of poly(MA) obtained from the photopolymerization of MA with phenylmethylsilane (mole ratio, 10 : 1).

ester linkage¹⁹ and then by the dehydration between two acid groups in the different polymer chains at around 250 °C, forming an acid anhydride linkage.²⁰ For the secondary silanes the little change of TGA residue yields at 400 °C of the poly(MA)s with increase of the relative silane concentration may suggest that the cross-linking by the formation of acid anhydride linkage should contribute by far more than the cross-linking by the formation of silyl ester linkage. The silyl ester linkage is known to be thermally weak. The cross-linking possibility might be slim on the photopolymerization conditions. The cross-linking processes could require high energy, which are anticipated only to occur during the pyrolysis.²¹ However, we should admit at this moment that we cannot completely exclude the low degree of cross-linking possibility during the photopolymerization.

In conclusion, this work describes the photopolymerization of MA with secondary silanes such as phenylmethylsilane and diphenylsilane. While the polymerization yields and intrinsic viscosities of the poly(MA)s containing the secondary silyl moieties decreased, the TGA residue yields and intensities of SiH stretching IR bands increased as the mole ratio of the secondary silanes over MA increased. The polymerizability of MA by the silyl radical seems to be naturally higher than that of MMA. The sterically less bulky silane PhMeSiH₂ afforded poly(MA)s with somewhat higher molecular weights and with similar TGA residue yields compared with the sterically bulkier silane Ph₂SiH₂. The secondary silyl moieties, once attached to the poly(MA) as an end group, could be left untouched before the pyrolysis occurring at high temperature. Other types of cross-linking process were suggested, based on the trend of the TGA residue yields. The secondary silanes appeared to competitively and concurrently function as both chain initiation and transfer agents in the photopolymerization of MA.

Acknowledgment. This research was supported by the Korea Science and Engineering Foundation (1995).

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