

Photopolymerization of Methyl Methacrylate with Disilanes

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The bulk photopolymerization of methyl methacrylate (MMA) with disilanes such as 1,2-diphenyldisilane and 2-phenyl-1,3-disilapropane was carried out to yield poly(MMA)s containing the corresponding disilyl moiety presumably as an end group. It was found that while the polymerization yields and the polymer molecular weights decreased as the relative disilane concentration increased, the TGA residue yields and the relative intensities of SiH IR stretching bands increased with increment of molar ratio of disilane over MMA. The photopolymerization of MMA with 2-phenyl-1,3-disilapropane produced higher-molecular-weight polymer with lower TGA residue yield when compared to the photopolymerization of MMA with 1,2-diphenyldisilane. The disilanes seemed to significantly influence on the photopolymerization as both chain initiation and chain transfer agents.

Introduction

Photopolymerization technology applicable conveniently is widely employed on a commercial scale today in the areas of surface coatings, photoresists, adhesives, and holography.¹ Although any vinyl monomer that will undergo chain reaction polymerization is 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. Methyl methacrylate is susceptible to direct photopolymerization on the exposure to 300 nm wavelength light. The detailed mechanism of the formation of the propagating radicals in this case 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

Hydrosilane is known to participate in versatile 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 intriguing types of silicon containing polymers such as dendrimers⁷ and copolymers.⁸ We already reported the bulk photopolymerization of MMA with primary silanes^{9a} and secondary silanes.^{9b} Here we report the bulk photopolymerization of MMA with disilanes such as 1,2-diphenyldisilane (PhH₂SiSiH₂Ph) and 2-phenyl-1,3-disilapropane (PhCH(SiH₃)₂) using 300 nm UV light to give poly(MMA)s containing the corresponding disilyl moiety presumably 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 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 Ultrastaygel 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⁻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 MgSO₄, and distilled at reduced pressure before use. 1,2-Diphenyldisilane and 2-phenyl-1,3-disilapropane were kindly provided by Prof. J. F. Harrod of McGill University and Dr. I. N. Jung of the Korea Institute of Science and Technology, respectively.

Bulk Photopolymerization of MMA with 2-Phenyl-1,3-disilapropane. Bulk photopolymerization of MMA with various molar ratio of 2-phenyl-1,3-disilapropane (10 : 1 through 3 : 7) was performed. 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 PhCH(SiH₃)₂ (0.30 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 0.36 g (18%) of benzene-soluble white solid (TGA residue yield at 400 °C: 10%). The polymer was characterized by ¹H NMR, IR, GPC, and TGA techniques. IR (KBr pellet, cm⁻¹): 2161 w (νSi-H), 1732 s (νC=O). ¹H NMR (δ, CDCl₃, 300 MHz): 0.7-1.1 (m, 3H, C-CH₃), 1.6-2.0 (m, CH and CH₂),

Table 1. Characterization of Photopolymerization of MMA with Disilanes^a

Silane	Mol ratio (MMA : Silane)	Yield (%)	Mol wt ^b		Relative intensity ^c IR (ν _{SiH})	TGA residue yield (%, at 400 °C)
			M _w	M _n		
PhCH(SiH ₃) ₂	10 : 1	18	132000	67100	1.0	10
	7 : 3	14	44700	22200	2.5	23
	5 : 5	8	22300	11600	3.0	34
	3 : 7	5	9400	6000	3.2	42
(PhSiH ₂) ₂	10 : 1	19	4800	2300	—	50

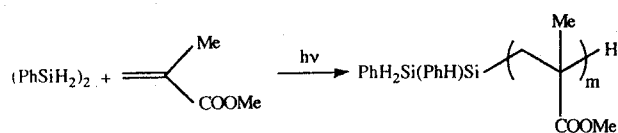
^aUV-irradiation for 6 h. ^bMeasured with GPC in THF. ^cRelative ratio with respect to the intensity of νSiH (MMA : Disilane = 10 : 1).

3.6 (m, 3H, OCH₃), 4.0-4.3 (m, SiH), 7.1-7.4 (m, ArH). GPC: M_w = 132000, M_n = 67100.

Bulk Photopolymerization of MMA with 1,2-Diphenyldisilane. A quartz test tube (1 cm × 20 cm) loaded with MMA (2.14 mL, 20 mmol) and PhH₂SiSiH₂Ph (0.43 g, 2.0 mmol) was degassed, sealed, and UV-irradiated for 6 h. The polymer was dissolved in toluene, precipitated in hexane, filtered off, and dried to afford 0.38 g (19%) of benzene-soluble white solid (TGA residue yield at 400 °C: 50%). The polymer was characterized by ¹H NMR, IR, GPC, and TGA techniques. IR (KBr pellet, cm⁻¹): 2133 w (νSi-H), 1730 s (νC=O). ¹H NMR (δ, CDCl₃, 300 MHz): 0.7-1.1 (m, 3H, C-CH₃), 1.7-2.2 (m, 2H, CH₂), 3.6 (m, 3H, OCH₃), 4.3-4.5 (m, SiH), 7.2-7.6 (m, ArH). GPC: M_w = 4800, M_n = 2300.

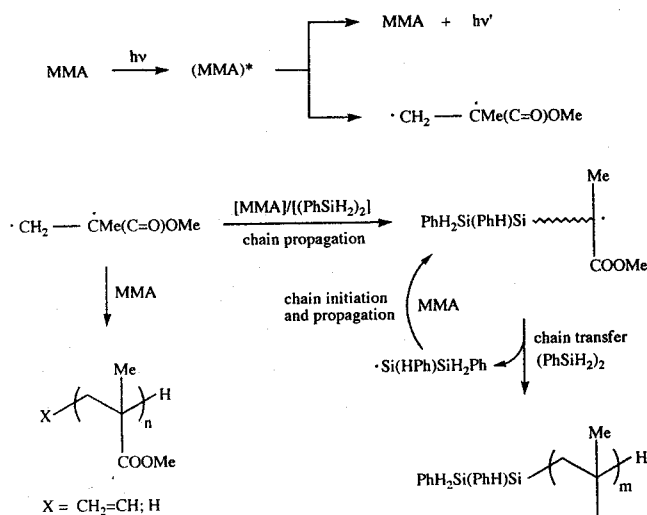
Results and Discussion

The poly(MMA) containing 1,2-diphenyldisilyl moiety with weight average molecular weight of 4800 and TGA residue yield of 50% was prepared in 19% yield by 300 nm UV light-initiated bulk polymerization of MMA with molar ratio of MMA : disilane = 10 : 1 (eq. 1).



Bulk photopolymerization of MMA with different molar ratio of 2-phenyl-1,3-disilapropane (MMA : disilane = 10 : 1 through 3 : 7) produced the poly(MMA)s containing the disilyl moiety with weight average molecular weights of 9400-132000 and TGA residue yields of 10-42% in 5-18% yields. The polymerization yields, relative IR intensities, GPC, and TGA data of the polymers are summarized in Table 1.

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.¹ The disilanes showed the similar trends as the other arylsilanes did. As shown in Table 1, while the polymerization yields and the polymer molecular weights decreased, the relative intensities of SiH IR stretching bands and the TGA residue yields increased as the molar ratio of disilane over MMA augmented. The resonances corresponding to the vinyl end groups were not observed in the ¹H NMR spectra of the poly(MMA)s even in the molar ratio of 10 : 1. We expect



Scheme 1. Postulated Mechanism for Photoreaction of MMA with 1,2-Diphenyldisilane.

the polymers to be produced in the molar ratio of 10 : <1 might be a mixture of two kinds of polymers with a vinyl end group or with a disilyl end group in view of the study on the photopolymerization of MMA with primary silanes.^{9a} The separation of two kinds of the polymers is technically hard because of their similar solubility. A detailed study for verifying this point is currently in progress using GPC and DSC analysis techniques.^{9c} We learned that hydrosilanes appear to help the photopolymerization of MMA.^{9b} These facts can be rationalized by Scheme 1. The absorption of light generates 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 yields 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 disilane 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 disilane concentration. The chain transfer might produce a disilyl radical which, in turn, leads to chain initiation, resulting in the production of poly(MMA) containing the disilyl moiety presuma-

bly as an end group.

It is uncertain why the chain propagation of MMA in the presence of silanes is facilitated when compared to the absence of silanes.⁹ We presume that the silanes could help the initiation of the polymerization and prevent some unidentified termination reaction from being occurred. The disilane somehow 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 disilanes for radical polymerization of MMA are not available, they could serve as an excellent chain transfer agent because PhSiH_3 has low Si-H bond energy of 88.2 kcal/mol¹⁰ 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.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

In the present study we employed two different types of disilanes to check whether they can serve as a cross-linking agent in the photopolymerization reaction of MMA. 1,2-Diphenyldisilane is an arylsilane with a direct Si-Si bond and 2-phenyl-1,3-disilapropane is an alkylsilane with a methylene spacer between two silicon atoms. We anticipated that the 1,2-diphenyldisilane might be a good cross-linking agent because the disilane has two silyl units and low Si-H bond energy due to the silyl substituent.^{3a} We aware the possibility of the Si-Si bond scission of the 1,2-diphenyldisilane under the 300 nm UV-irradiation condition. However, we believe the disilane oligomer unlike polysilanes should have the much less chance of the Si-Si bond scission. We also expected that the 2-phenyl-1,3-disilapropane will produce a poly(MMA) in as low yield as the alkylsilane $\text{PhCH}_2\text{SiH}_3$ does in the photopolymerization reactions. Interestingly, the photopolymerization of MMA with $\text{PhCH}(\text{SiH}_3)_2$ possessing an extra electron-donating SiH_3 group gave the poly(MMA)s in greater yield than with $\text{PhCH}_2\text{SiH}_3$ (18% vs. 2%).^{9a} The photopolymerization of MMA with 2-phenyl-1,3-disilapropane produced higher-molecular-weight and lower-TGA-residue-yield polymers when compared to the photopolymerization of MMA with 1,2-diphenyldisilane. The photopolymerization of MMA with 2-phenyl-1,3-disilapropane afforded poly(MMA)s with similar molecular weights, TGA ceramic yields, and polymerization yields compared to the photopolymerization of MMA with secondary silanes such as PhMeSiH_2 and Ph_2SiH_2 .^{9b} The Si-H bond energies of silanes are known to be mostly uniform except 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 a silane, but the substitution of phenyl group increases it.¹³ The disilane $\text{PhCH}(\text{SiH}_3)_2$ seemed to have the higher cross-linking chance (due to smaller steric effect and more Si-H bonds) and the lower inclination of chain transfer (due to weaker hydrogen donation ability) than the disilane $\text{PhH}_2\text{SiSiH}_2\text{Ph}$ in view of the data of Table 1. In consideration of the following items: (1) the trend of solubility, polymerization yields, and molecular weight distributions with variation of disilane 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 disilyl end groups in the other polymer chains might be scanty. The cross-linking process could require high energy, which is anticipated only to occur during the pyrolysis.¹⁴ However, we should admit at this moment that we cannot exclude the cross-linking possibility completely.

In conclusion, this work describes the bulk photopolymerization of MMA with arylidisilane and alkylidisilane. Poly(MMA)s containing disilyl end group with molecular weights of 4800-132000 and TGA residue yields of 10-50% were obtained in 5-19% yields. While the polymerization yields and the molecular weights of the poly(MMA)s containing disilyl moieties decreased, the TGA residue yields and relative intensities of SiH stretching IR bands increased as the molar ratio of disilane over MMA increased. The photopolymerization of MMA with 2-phenyl-1,3-disilapropane produced higher-molecular-weight polymers having lower TGA residue yield when compared to the photopolymerization of MMA with 1,2-diphenyldisilane. The disilyl moieties, once attached to the poly(MMA) as end group, could be left untouched before the pyrolysis occurring at high temperature. The disilanes 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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The Binding Energy of HIV-1 Protease Inhibitor

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The potential energies of HIV-1 protease, inhibitor, and their complex have been calculated by molecular mechanics and the "binding energy", defined as the difference between the potential energy of complex and the sum of potential energies of HIV-1 protease and its inhibitor, has been compared to the free energy in inhibition reaction. The trend in these binding energies seems to agree with that in free energies.

Introduction

The etiological agent of AIDS has been identified as human immunodeficiency virus (HIV), and two genetically distinct subtypes, HIV-1 and HIV-2, have been characterized.^{1,2} There are many kinds of possibilities in blocking the normal multiplication of HIV-1. One of those methods is to block the normal action of HIV-1 protease so that HIV-1 protease can not effectively make regulatory proteins, structural proteins and maturation proteins from their precursor, polyprotein. HIV-1 protease is consisted of two monomer units each of which has completely the same amino acid sequence of 99 residues as shown in Figure 1 and has C₂ symmetric axis within it as shown in Figure 2.

Several types of HIV-1 protease inhibitors are suggested and investigated by many authors. One of the classical strategies for designing enzyme inhibitors relies on incorporating a transition-state mimic into substrate analogues. Refinements of this strategies, in which nonhydrolyzable dipeptide isosteres were substituted for the scissile amide bond in an appropriate sequence context, proved highly successful for producing potent renin inhibitor.³ Figure 3 shows inhibitors which is used in our calculation.

Many researchers have tried to develop new inhibitors with better activities. The proper descriptor of activity may relieve an effort of the development but the current methods do not give satisfactory results for the development of new inhibitor, especially which has substantially different structure from the existing inhibitors. So we tried to define the physical quantity which is computable simply, applicable to various inhibitors and predictable qualitative trends of activity and investigated the quantity with available data set.

PRO GLN ILE THR LEU TRP GLN ARG PRO LEU VAL THR ILE
 LYS ILE GLY GLY GLN LEU LYS GLU ALA LEU LEU **ASP** THR
 GLY ALA ASP ASP THR VAL LEU GLU GLU MET ASN LEU PRO
 GLY ARG TRP LYS PRO LYS MET ILE GLY GLY ILE GLY GLY
 PHE ILE LYS VAL ARG GLN TYR ASP GLN ILE LEU ILE GLU
 ILE CYS GLY HIS LYS ALA ILE GLY THR VAL LEU VAL GLY
 PRO THR PRO VAL ASN ILE ILE GLY ARG ASN LEU LEU THR
 GLN ILE GLY CYS THR LEU ASN PHE

Figure 1. Amino acid sequence of HIV-1 protease which was derived from bacterial expression. The six underlined residues are different amino acids from corresponding synthetic protease. The 25th residue, ASP in boldface is very important in the catalytic hydrolyzation of polyprotein.

Methods

Inhibition constant, K_i , for the equilibrium between the enzyme and inhibitor, is defined as follows:

$$EI \rightleftharpoons E + I \quad (1)$$

$$K_i = \frac{[E][I]}{[EI]} \quad (2)$$

The inhibitor which has smaller K_i bind more tightly to its target. Since K_i is obtained through biological assays, *in vitro* experiments, the synthesis of inhibitor is prerequisite to its test. Therefore, even crude, the prediction of the potency of artificial inhibitor, is preferable in alleviating efforts of syntheses. In present work, we tried to find the physical quantities which describe the inhibition constant properly and which can be calculated by theoretical computation even before synthesis.