Photopolymerization of Methyl Methacrylate with Disilanes

Hee-Gweon Woo*, Lan-Young Hong, Jin-Young Park, Young-Tae Jeong,
Hyung-Ryun Park, and Heu-Suk Ham

Department of Chemistry, Chonnam National University, Kwanju 500-757, Korea
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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 Si–H 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. 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.

Hydrosilane is known to participate in versatile reactions such as free radical reduction of organic halides, nucleophilic reduction of carbonyl compounds, dehydrogenative Si-Si coupling, and hydrosilation of olefins with catalyst. The hydrosilation has been used to prepare many intriguing types of silicon containing polymers such as dendrimers and copolymers. We already reported the bulk photopolymerization of MMA with primary silanes and secondary silanes. 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 form 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, 106, 105, 104 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 Rayonet 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 0.26 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 (vSiH); 1732 s (vC=O). 1H NMR (6, 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*

<table>
<thead>
<tr>
<th>Silane</th>
<th>Mol ratio (MMA : Silane)</th>
<th>Yield (%)</th>
<th>Mol wt(^1) (M_n)</th>
<th>Relative intensity(^2) IR ((\nu_{SiH}))</th>
<th>TGA residue yield (%, at 400 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhCH(SiH)(_2)</td>
<td>10 : 1</td>
<td>18</td>
<td>132000 67100</td>
<td>1.0</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>7 : 3</td>
<td>14</td>
<td>44700 22200</td>
<td>2.5</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>5 : 5</td>
<td>8</td>
<td>22300 11600</td>
<td>3.0</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>3 : 7</td>
<td>5</td>
<td>9400 6000</td>
<td>3.2</td>
<td>42</td>
</tr>
<tr>
<td>(PhH)Si(_2)</td>
<td>10 : 1</td>
<td>19</td>
<td>4800 2300</td>
<td>-</td>
<td>50</td>
</tr>
</tbody>
</table>

*UV-irradiation for 6 h. \(^1\)Measured with GPC in THF. \(^2\)Relative ratio with respect to the intensity of vSiH (MMA : Disilane=10 : 1).

3.6 (m, 3H, OCH\(_3\)), 4.0-4.3 (m, SiH), 7.1-7.4 (m, ArH). GPC: \(M_n=132000, M_w=67100\).

**Bulk Photopolymerization of MMA with 1,2-Diphenyldisilane.** A quartz test tube (1 cm\(\times\)20 cm) loaded with MMA (2.14 mL, 20 mmol) and PhH\(_2\)Si(SiH)\(_2\)Ph (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 \(^1\)H NMR, IR, GPC, and TGA techniques. IR (KBr pellet, cm\(^{-1}\)): 2133 w (vSi-H), 1730 s (vC=O), \(^1\)H NMR (6, CDCl\(_3\), 300 MHz): 0.7-1.1 (m, 3H, C-CH\(_3\)), 1.7-2.2 (m, 2H, CH\(_2\)), 3.6 (m, 3H, OCH\(_3\)), 4.3-4.5 (m, SiH), 7.2-7.6 (m, ArH). GPC: \(M_n=4800, M_w=2300\).

**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).

![Structure of MMA](attachment:image.png)

Bulk photopolymerization of MMA with different molar ratio of 2-phenyl-1,3-disilapropylene (MMA : disilane=10 : 1 through 3 : 7) produced the poly(MMAs) 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 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 \(^1\)H NMR spectra of the poly(MMAs) even in the molar ratio of 10 : 1. We expect 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.\(^{2}\) The separation of two kinds of the polymers is technologically hard because of their similar solubility. A detailed study for verifying this point is currently in progress using GPC and DSC analysis techniques.\(^{3}\) We learned that hydrosilanes appear to help the photopolymerization of MMA.\(^{4}\) 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 near 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-
by 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. 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 PbSiH₂ has low Si-H bond energy of 88.2 kcal/mol 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. 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.

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-Di-phenyldisilane 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-diphenylsilane 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. We aware the possibility of the Si-Si bond scission of the 1,2-diphenylsilane 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 PhCH₂SiH₃ does in the photopolymerization reactions. Interestingly, the photopolymerization of MMA with PhCH₂SiH₃ possessing an extra electron-donating SiH₂ group gave the poly(MMA)s in greater yield than with PhCH₂SiH₃ (18% vs. 2%). 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-diphenylsilane. 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 PhMeSiH₂ and Ph₂SiH₃. The Si-H bond energies of silanes known to be mostly uniform except silanes with strongly electron-withdrawing and/or silyl substituents in the α-position. 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. The disilane PhCH(SiH₃)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 Ph₂SiH₂Ph 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 alky 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. 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 arylsilane and alkylsilane. 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-diphenylsilane. 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. Acknowledgment. This research was supported by the Korea Science and Engineering Foundation (1995).

References

The Binding Energy of HIV-1 Protease Inhibitor

Jaejin Ka, Sang-Hyun Park, and Hojung Kim

Department of Chemistry, Seoul National University, Seoul 151-742, Korea
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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. 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 cannot 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 C3 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. 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  ASP  THR  GLY  ALA  ASP  ASP  THR  VAL  LEU  GLU  GLU  MET  ASN  LEU  PRO  GLY  ARG  TRP  LYS  PRO  LYS  MET  ILE  GLY  ILE  GLY  GLY  GLY  PHE  ILE  LYS  VAL  ARG  GLN  TYR  ASP  ASN  ILE  LEU  ILE  GLU  ILE  GLY  HIS  LYS  ALA  ILE  GLY  THR  VAL  LEU  VAL  GLY  PRO  THR  PRO  VAL  ASP  ILE  ILE  GLY  ARG  ASH  LEU  LEU  LEU  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:

$$EI \leftrightarrow E + I$$

(1)

$$K_i = \frac{[EI]}{[E][I]}$$

(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.