Photopolymerization of Methacrylic Acid with Phenylsilane

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The bulk photopolymerization of methacrylic acid (MA) with phenylsilane was performed to produce poly(MA)s containing phenylsilyl 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 molar ratio of phenylsilane over MA. The phenylsilane seemed to significantly influence on the photopolymerization as both chain initiation and chain transfer agents.

Introduction

Widely various unsaturated vinyl derivatives can undergo free-radical chain polymerization. The ability to perform a thermodynamically possible polymerization relies upon its kinetic feasibility on whether the process proceeds at a reasonable rate under a given set of reaction conditions. Initiator or promoter are often required to achieve the kinetic feasibility. Photopolymerization technology applicable conveniently is amply used on a commercial basis today in the areas of surface coatings, photoresists, adhesives, and holography. Although any vinyl derivative that will undergo chain polymerization is basically 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 of the formation of the propagating radicals in this case is not thoroughly 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 can partake in versatile reactions such as free radical reduction of organic halides, nucleophilic reduction of carbonyl compounds, dehydropolymerization, cross-dehy-
drcoupling, and hydrosilation of olefins with catalyst. The hydrosilation has been applied to prepare many intriguing types of silicon containing polymers such as dendrimers and copolymers. We reported the bulk photopolymerization of methyl methacrylate (MMA) with various silanes. Here we report the bulk photopolymerization of methacrylic acid (MA) with phenylsilane to give poly(MA)s containing phenylsilyl moiety presumably as an end group.

**Experimental Section**

**Materials and Instrumentation.** All reactions and manipulations were carried out under purified 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 DMSO-d$_6$/DMSO-H$_2$O as a reference at 2.49 ppm downfield from TMS. Reduced viscosity ($\eta_{\text{red}}$) and inherent viscosity ($\eta_{\text{inh}}$) of different concentrations ($c$ in g/dL) of polymer solutions in DMF were obtained by measuring three successive readings of the efflux time (polymer, $t_1$; solvent, $t_0$) with Ostwald-Fenske viscometer immersed in the constant-temperature bath maintaining at 25$\pm$0.01 $^\circ$C and by substituting the mean of three readings into the known equations. The extrapolation of the two viscosities to the same intercept as $c$ approached to zero gave the intrinsic viscosity ($\eta_\text{in}$) 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 $^\circ$C, at a rate of 10 $^\circ$C/min. TGA residue yield (for convenience sake, read at 400 $^\circ$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=6.83$\times$10$^{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. PhSiH$_3$ was prepared by reduction of PhSiCl$_3$ (Hils America Inc.) with LiAlH$_4$ in diethyl ether.

**Bulk Photopolymerization of MA with Phenylsilane.** Bulk photopolymerization of MA with different molar ratio of PhSiH$_3$ (10 : 1 through 3 : 7) was carried out. In a typical experiment, a quartz test tube (1 cm$\times$20 cm) charged with MA (1.72 g, 20 mmol) and PhSiH$_3$ (0.22 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 1.90 g (98%) of white solid (TGA residue yield at 400 $^\circ$C: 66%). $^1$H NMR (5, DMSO-d$_6$, 300 MHz): 0.9-1.1 (br, 3H, C-CH$_3$), 1.8-2.1 (br, 2H, CH$_2$), 7.2-7.8 (m, ArH), 12.3 (br, 1H, OH). The SiH resonance was not clearly observed in the $^1$H NMR spectrum. IR (KBr pellet, cm$^{-1}$): 3400 br s ($\nu_{\text{OH}}$), 2142 w ($\nu_{\text{SiH}}$), 1705 s ($\nu_{\text{C=O}}$). Intrinsic viscosity: 0.99 dL/g. As a control experiment, bulk photopolymerization of MA without PhSiH$_3$ for 6 h produced poly(MA) (TGA residue yield at 400 $^\circ$C: 18%); Intrinsic viscosity: 0.50 dL/g in small amount after precipitation.

**Results and Discussion**

The poly(MA)s containing phenylsilyl moiety with intrinsic viscosities of 0.53-0.99 dL/g and TGA residue yields of 66-69% were prepared in 15-58% yields by bulk photopolymerization of MA with different molar ratio of phenylsilane (MA : phenylsilane=10 : 1 through 3 : 7) (eq. 1).

$$\text{PhSiH}_3 + \text{COOH} \xrightarrow{\text{hv}} \text{PhH}_2\text{Si} + \text{COOH}$$

PhSiH$_3$ + COOH $\xrightarrow{\text{hv}}$ PhH$_2$Si + COOH

The polymers were soluble in DMF, DMSO, and methanol. The characterization data of the resulting poly(MA)s are summarized in Table 1.

<table>
<thead>
<tr>
<th>Mol ratio (MA : Silane)</th>
<th>Yield (%)</th>
<th>Intrinsic viscosity$^a$ [η]</th>
<th>Relative intensity$^b$ IR (ν$_{\text{SiH}}$) (% at 400 $^\circ$C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10:1</td>
<td>98</td>
<td>0.99</td>
<td>1.0</td>
</tr>
<tr>
<td>7.3</td>
<td>72</td>
<td>0.93</td>
<td>1.2</td>
</tr>
<tr>
<td>5:5</td>
<td>49</td>
<td>0.87</td>
<td>1.7</td>
</tr>
<tr>
<td>3:7</td>
<td>15</td>
<td>0.53</td>
<td>2.0</td>
</tr>
</tbody>
</table>

$^a$UV-irradiation for 6 h. $^b$Measured in DMF at 25 $^\circ$C; unit, dL/g. $^c$Relative ratio with respect to the intensity of ν$_{\text{SiH}}$ (MA : Phenylsilane=10 : 1).

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. The intrinsic viscosity is directly related to the weight average molecular weight of polymer. As shown in Table 1, while the polymerization yields and intrinsic viscosities decreased, the relative intensities of SiH IR stretching bands and TGA residue yields increased as the molar ratio of silane over MA augmented. It is worth to note that the intrinsic viscosity and polymerization yield with phenylsilane for the photopolymerization of molar ratio of MA : phenylsilane=10 : 1 were much higher than without phenylsilane. These facts can be rationalized as follows (vide infra). The absorption of light may produce an 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. At near 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 chain propagation with increasing phenylsilane 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 phenylsilyl moiety as an end group as shown in Scheme 1. Polysilyl radicals generated from the photochemical homolysis of polysilanes are known to be able to initiate the free-radical chain polymerization of some vinyl monomers. Phenylsilane 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 phenylsilane for radical polymerization of MA are not available, it could serve as an excellent chain transfer agent because PhSiH₃ 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 triphenylsiline. In the present study we used phenylsilane which is an arylsilane without methylene spacer between phenyl group and silicon center. We described the photopolymerization of MMA with aryl-substituted alkylsilanes, 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. Aryl group-free alkylsilanes also showed a negligible effect on the photopolymerization of MMA. 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. 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. 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 first receives 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, the MA polymerization yield were higher than the MMA polymerization yield. 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 phenylsilane were much higher than those of poly(MMA)s with phenylsilane. The change of the TGA residue yields of the poly(MA)s with increasing the relative phenylsilane concentration was very little when compared to that of the poly(MMA)s. Interestingly, 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 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 ester linkage and then by the dehydration between two acid groups in the different polymer chains at around 250 °C, forming an acid anhydride linkage. The little change of the TGA residue yields at 400 °C of the poly(MA)s with increasing the relative phenylsilane 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. In consideration of the following items: (1) the trend of solubility, polymerization yields, and intrinsic visco-
sities 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 might be slim. The cross-linking processes could require high energy, which are anticipated only to occur during the pyrolysis. However, we should admit at this moment that we cannot completely exclude the low degree of cross-linking possibility.

In conclusion, this work describes the photopolymerization of MA with phenylsilane. While the polymerization yields and intrinsic viscosities of the poly(MAs) containing phenylsilyl moieties decreased, the TGA residue yields and intensities of SiH stretching IR bands increased as the molar ratio of phenylsilane over MA increased. The phenylsilyl moieties, once attached to the poly(MA) as an end group, could be left untouched before the pyrolysis occurring at high temperature. Another type of cross-linking process was suggested, based on the trend of the TGA residue yields. The phenylsilane appeared to competitively and concurrently function as both chain initiation and transfer agents in the polymerization of MA.

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References