

# PHENYLSILANS와 2-HYDROXYETHYL METHACRYLATE의 열중합

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Poly(HEMA)는 소프트 콘택트렌즈의 재료로써 널리 사용되어 왔다.  $\text{phSiH}_3$ ,  $\text{phMeSiH}_2$ ,  $\text{ph}_2\text{SiH}_2$ 와 같은 다양한 hydrosilane들과 hydroxyethyl methacrylate(HEMA)와의 열중합은 Phenylsilyl 말단을 포함하는 poly(HEMA)를 생성시켰다. 열중합 반응 동안에는 Phenylsilane의 농도가 증가함에 따라 고분자의 분자량과 고분자 수득률이 감소됨을 보였으며 광중합 반응에서 보다 중합 수득률, 고분자의 분자량, TGA 잔여 수율 등이 더 높았다.

## THERMAL POLYMERIZATION OF 2-HYDROXYETHYL METHACRYLATE WITH PHENYLSILANS

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Poly(HEMA)s have been used as the optometric material for the preparation of soft contact lens. The bulk thermal polymerization of 2-hydroxyethyl methacrylate (HEMA) with various hydrosilanes such as  $\text{phSiH}_3$ ,  $\text{phMeSiH}_2$ , and  $\text{ph}_2\text{SiH}_2$  were performed to produce poly(HEMA)s containing phenylsilyl end moiety. It was found for thermal polymerization that while the polymerization yield and polymer molecular weights decreased as the relative phenylsilane concentration increases, the TGA residue yields and the relative intensities of SiH IR stretching bands increased as the relative hydrosilane concentration increases over HEMA. The polymerization yield, molecular weight, and TGA residue for the thermal polymerization were higher than those for the photo polymerization. Thus, the hydrosilanes significantly influence on the polymerization as both chain-initiation and chain-transfer agents.

### I Introduction

A wide variety of unsaturated vinyl derivatives can be induced to undergo free-radical chain polymerization.<sup>[1]</sup> The capability to carry out a thermodynamically feasible polymerization relies on its kinetic feasibility on whether the process proceeds at a reasonable rate under a given set of reaction conditions. Initiator or promotor are often required to achieve the kinetic feasibility. Convenient

and clean photo polymerization technology is extensively used for commercial application in the versatile areas of surface coatings, photoresists, adhesives, and holography.<sup>[1]</sup> Only a few unsaturated monomers including methyl methacrylate (MMA) are known to absorb light between 250 and 500 nm which is the most convenient wavelength range for common experimental work. Although the detailed mechanism of photochemically forming the propagating radicals is not thoroughly understood, it seems to involve the excited triplet state.<sup>[2]</sup> Hydrosilane

is known to participate in versatile reactions such as free radical reduction of organic halides,<sup>[3]</sup> nucleophilic reduction of carbonyl compounds,<sup>[4]</sup> dehydropolymerization,<sup>[5]</sup> crossdehydrocoupling,<sup>[6]</sup> and hydrosilation of olefins<sup>[7]</sup> with catalyst. Heating (thermal energy) can be used to make many interesting types of silicon containing polymers such as dendrimers<sup>[8]</sup> and copolymer.<sup>[9]</sup> Various rigid poly (HEMA) products, such as sheet, rod, and tube, are produced by bulk polymerization in a casting process.

## II Experimental

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 under the same conditions such as cell thickness, sample concentration, etc. using a Nicolet 520P FT-IR spectrometer. Proton NMR spectra were recorded on a Bruker ASX 32 (300 MHz) spectrometer using CDCl<sub>3</sub>/CHCl<sub>3</sub> as a reference at 7.24 ppm downfield from TMS. 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. Bulk thermal polymerization of 2-hydroxyethyl methacrylate (HEMA) with different molar ratio of hydrosilanes such as  $\text{PhSiH}_3$ ,  $\text{PhMeSiH}_2$ ,  $\text{Ph}_2\text{SiH}_2$  (9 : 1 through 1 : 9) was carried out. In a typical experiment, a glass test tube (1 cm × 20 cm) containing with HEMA (1.1 g, 8.5 mmol) and  $\text{PhSiH}_3$  (0.1 g, 0.92 mmol) was degassed, sealed, and heated at 70°C for 10 h. The polymer was dissolved in toluene, precipitated in hexane, filtered off, and dried to give 1.16 g (96%) of white solid (TGA residue yield at 600°C : 4%). For the thermal polymerization experiments a thermostat bath (model SVM-67) made by the Samik Scientific Co. The polymer was characterized by NMR, IR, TGA, and viscosimeter techniques. IR (KBr pellet,  $\text{cm}^{-1}$ ) : 2170w ( $\nu$  Si-H), 1728s ( $\nu$  C=O).

## III Result and Discussion

The poly(HEMA)s possessing phenylsilyl moiety with TGA residue yields of 4~22% were synthesized in 14~96% yields by bulk thermal polymerization of HEMA with varying the molar ratio of phenylsilane (HEMA : phenylsilane = 1 : 9 through 9 : 1). (eq. 1) The characterization data are summarized in Table 1. The data of phenylmethyl silane, diphenylsilane are shown in Table 2, 3.

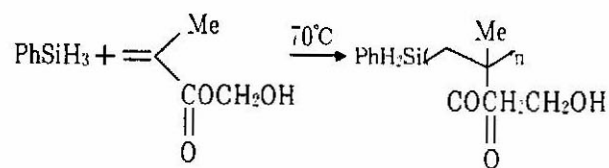
Table 1. Thermal Polymerization of HEMA with Phenylsilane.

Mol ratio (PhSiH <sub>3</sub> : HEMA)	Yield (%)	Relative intensity IR ( $\nu$ Si-H)	TGA residue yield (% at 600°C)	Inherent viscosity [ $\eta$ ]
9 : 1	14	6.5	22	-
7 : 3	49	4.6	19	0.53
5 : 5	70	2.9	8	0.65
3 : 7	81	2.6	6	0.76
1 : 9	96	1.5	4	1.00

Heating at 70°C for 10 hr.

Relative ratio with respect to the intensity of  $\nu$  Si-H  
(silane : HEMA = 1 : 9).

Measured in DMF at 25°C.



eq. 1

It is well known that high-molecular-weight polymer is formed immediately and that the weight average molecular weight increase of polymerization yield in the radical polymerization of vinyl monomers. As shown in Table 1, 2 and 3 for thermal polymerization while the

**Table 2.** Thermal Polymerization of HEMA with Phenylmethylsilane

Mol ratio (PhSiH : HEMA)	Yield(%)	Relative intensity IR( $\nu$ Si-H)	TGA residue yield (% at 600 °C)	Inherent viscosity [ $\eta$ ]
9 : 1	5	3.2	9	
7 : 3	38	2.3	8	0.44
5 : 5	63	1.9	6	0.55
3 : 7	87	1.3	4	0.65
1 : 9	99	1.0	2	0.89

Heating at 70°C for 10 hr.

Relative ratio with respect to the intensity of  $\nu$  Si-H

(silane : HEMA = 1 : 9)

Measured in DMF at 25°C.

**Table 3.** Thermal Polymerization of HEMA with Diphenylsilane.

Mol ratio (PhSiH : HEMA)	Yield(%)	Relative intensity IR( $\nu$ Si-H)	TGA residue yield (% at 600°C)	Inherent viscosity [ $\eta$ ]
9 : 1	9	6.1	-	-
7 : 3	28	5.0	8	0.53
5 : 5	52	3.9	6	0.59
3 : 7	73	2.8	3	0.75
1 : 9	99	1.0	2	1.11

Heating at 70°C for 10 hr.

Relative ratio with respect to the intensity of  $\nu$  Si-H

(silane : HEMA = 1 : 9)

Measured in DMF at 25°C.

polymerization yields decreased, the relative intensities of SiH IR stretching bands and TGA residue yields increased as the molar ratio of silane over HEMA augmented. It should be also noted that polymerization yield with phenylsilane for the thermal polymerization of molar ratio of HEMA : silane = 9 : 1 were much higher than without phenylsilane. In other words, the phenylsilane apparently helps the thermal polymerization of HEMA until the molar ratio of HEMA : silane reaches at 9, but to hamper the reaction after the molar ratio with increase of phenylsilane concentration. The absorption of heat may produce an excited singlet state of

HEMA which will either fluoresce or be converted to an excited state, diradical of HEMA monomer. Attack on the other HEMA by this diradical affords a new diradical of HEMA dimer which either reverts to the ground state two HEMA molecules or attacks on the other HEMA that ultimately initiate polymerization. At neat condition the latter will be a predominant process to produce poly(HEMA) radicals. At high HEMA or low silane concentrations, chain propagation will be able to compete with chain transfer over the poly(HEMA) radicals. However, the chain transfer will eventually rule over chain propagation with increase of silane concentration. The chain transfer might produce a silyl radicals which, in turn, leads to chain initiation, resulting in the production of poly(HEMA) containing the silyl moiety as an end group.

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 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 fluorphotometer.

## IV Conclusion

In conclusion, This work describes the thermal polymerization of HEMA with silane. The polymer molecular weight (by viscosity measurement) and polymerization yields decrease, the TGA residue yields and IR intensities of Si-H stretching bands increase with increase of molar ratio of silane over HEMA. The hydro-silanes competitively and concurrently act as both chain-initiation and chain-transfer agents in the thermal polymerization of HEMA.

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