
PHENYLSILANE의 존재하에서 HEMA(2-Hydroxyethylmethacrylate)의 중합

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Phenylsilane들과 2-Hydroxyethylmethacrylate(HEMA)의 광중합은 말단기에 phenylsilyl기를 포함하고 있는 poly(HEMA)s를 생성시킴으로써 열중합과 같은 결과를 보였다. 중합반응 동안에 실란의 플비율이 증가함에 따라 중합수율과 고유점도는 감소하였으며, TGA 잔여수율과 Si-H IR 신축띠의 상대적 세기는 증가하는 경향을 보였다. phenylsilane는 HEMA와의 광중합 반응에서 연쇄개시제와 전달물질로 중요한 영향을 주었다.

POLYMERIZATION OF HEMA IN THE PRESENCE OF PHENYLSILANES

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The bulk photopolymerization of 2-hydroxyethylmethacrylate(HEMA) with phenylsilane was performed to produce poly(HEMA)s containing phenylsilyl moiety presumably as an end group. This results are the same as that of thermal polymerization. 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 HEMA. The phenylsilane seemed to significantly influence on the photopolymerization as both chain initiation and chain transfer agents.

I Introduction

Light-initiated polymerization of vinyl monomers has received a considerable amount of attention due to its several merits. The most obvious advantages might be the marked convenience and avoidance of chemical contamination by initiator residues. 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 and 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 halography^[1]. 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 wave-

length range for experimental work. The detailed mechanism of formation of the propagating radicals in this case is not thoroughly understood, but it appears to involve the conversion of electronically excited singlet state of the monomer to a long-lived excited triplet state^[2]. Hydrosilane can partake in versatile such as free radical reduction of organic halides^[3], nucleophilic reduction of carbonyl compounds^[4], dehydropolymerization^[5], cross dehydrocoupling^[6], 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^[7]. Here report the bulk photo polymerization of 2-hydroxyethylmethacrylate(HEMA) with phenylsilane to give poly(HEMA)s containing phenylsilyl moiety presumably as an end group.

II Experimental

1. Materials and Instrumentation

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 used. The built-in monochromatic UV-light sources(RUL- 300 nm UV lamp: lamp intensity = $6.93 \times 10^{13} \text{ h}\nu \text{ mL}^{-1}\text{min}^{-1}$) was positioned approximately 17 cm from the reaction quartz tube. All reactions and manipulations were carried out under prepurified nitrogen using Schlenk techniques. Dry, oxygen-free solvents were employed throughout. PhSiH₃ was prepared by reduction of PhSiCl₃ with LiAlH₄ in diethyl ether^[8]. Glassware was flame-dried or oven dried before use. Infrared spectra were obtained using a Nicolet 520P FT-IR spectrometer. Intrinsic viscosity of different concentration of polymer solutions in DMF were obtained by measuring three satisfactory readings of the efflux time(polymer, t; solvent, t₀) with Ostwald-Fenske viscometer immersed in the constant-temperature bath maintaining at $25 \pm 0.01^\circ\text{C}$ and by substituting the mean of three readings into the known equation^[9]. The extrapolation of the two vis-cosities to the same intercept as c approached to zero gave the intrinsic viscosity $[\eta]$

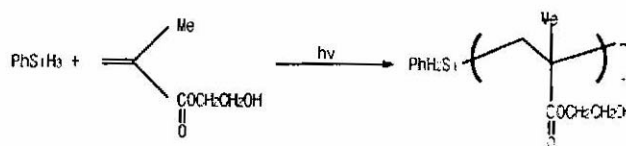
in dL/g. Thermogravimetric analysis(TGA) of polymer sample was performed on a Perkin Elmer 7 Series thermal analysis system under a nitrogen flow(50 mL/min). The polymer sample was heated from 25 to 700°C, at a rate of 10°C/min. TGA residue yield is reported as a percentage of the sample remaining after completion of the heating cycle.

2. Bulk photopolymerization of HEMA with phenylsilane.

Bulk photopolymerization of HEMA with different molar ratio of hydrosilanes(9:1 through 1:9) were carried about. The following procedure is representative of the photopolymerization reactions. A quartz test tube(1 cm × 20 cm) charged with HEMA(1.10 g, 8.5 mmol) and PhSiH₃(0.10 g, 0.92 mmol) was degassed, sealed, and irradiated with 250 nm UV-light for 10 h.

III Result and Discussion

The poly(HEMA)s containing phenylsilyl moiety with intrinsic viscosities of 0.26~0.70 dL/g and TGA residue yields of 2~10% were prepared in 8~83% yields by bulk photopolymerization of HEMA with different molar ratio of phenylsilane(HEMA:phenylsilane=9:1 through 1:9) (eq 1)



The polymers was taken in toluene, precipitated in hexane, filtered off, and dried to give 0.99 g(83%) of white solid(TGA residue yield at 600°C : 2%) The polymer was characterized by IR, TGA, and viscometer techniques. IR(KBR pellet, cm^{-1}): 2170 w($\nu_{\text{Si-H}}$), 1728 s($\nu_{\text{C=O}}$). The characterization data are summarized in table 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

Table 1. Characterization of Photopolymerization of HEMA with PhSiH₃.^a

Mol ratio (HEMA:PhSiH ₃)	Yield (%)	Relative intensity ^b IR(ν_{Si-H})	TGA residue Yield (%, at 600°C)	Intrinsic Viscosity ^c [η]
1:9	8	3.9	10	0.26
3:7	28	2.5	5	0.55
5:5	51	1.8	4	0.58
7:3	74	1.4	3	0.65
9:1	83	1.0	2	0.70

^aUV-Irradiation for 10 hr.

^bRelative ratio with respect to the intensity of ν_{Si-H}
(HEMA:Silane = 9:1).

^cMeasured in DMF at 25°C.

Table 2. Characterization of Photopolymerization of HEMA with PhMeSiH₂.^a

Mol ratio (HEMA:PhSiH ₃)	Yield (%)	Relative intensity ^b IR(ν_{Si-H})	TGA residue Yield (%, at 600°C)	Intrinsic Viscosity ^c [η]
1:9	6	1.6	10	0.43
3:7	30	1.3	8	0.61
5:5	50	1.2	7	0.88
7:3	71	1.1	5	1.14
9:1	80	1.0	4	1.38

^aUV-Irradiation for 10 hr.

^bRelative ratio with respect to the intensity of ν_{Si-H}
(HEMA:Silane = 9:1).

^cMeasured in DMF at 25°C.

Table 3. Characterization of Photopolymerization of HEMA with Ph₂SiH₂.^a

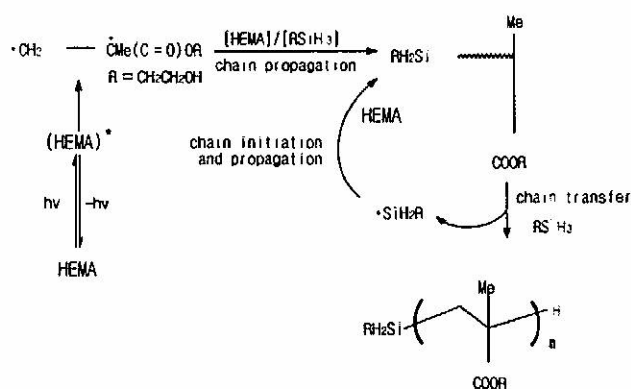
Mol ratio (HEMA:PhSiH ₃)	Yield (%)	Relative intensity ^b IR(ν_{Si-H})	TGA residue Yield (%, at 600°C)	Intrinsic Viscosity ^c [η]
1:9	16	4.1	30	0.64
3:7	36	3.0	12	0.70
5:5	52	2.9	7	0.77
7:3	74	2.1	4	0.87
9:1	92	1.0	2	0.89

^aUV-Irradiation for 10 hr.

^bRelative ratio with respect to the intensity of ν_{Si-H}
(HEMA:Silane = 9:1).

^cMeasured in DMF at 25°C.

The intrinsic viscosity is directly related to the weight average molecular weight of polymer^[9]. As shown in Table 1.2 and 3. While the polymerization yield and intrinsic viscosities decreased, the relative intensities of SiH IR stretching bands and TGA residue yields increased as the molar ratio of silane over HEMA augmented. It is worth to note that the intrinsic viscosity and polymerization yield with phenylsilane for the photopolymerization of molar ratio of HEMA:phenylsilane = 9:1 were much higher than without phenylsilane. These facts can be rationalized as follows. The absorption of light may produce an excited singlet state of HEMA which will either fluoresce or be converted to an excited and long lived triplet 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 increasing phenylsilane concentration. The chain transfer might produce a silyl radical which, in turn, leads to chain initiation, resulting in the production of poly(HEMA) containing the phenylsilyl moiety as an end group as shown in scheme 1^[10]. Polysilyl radicals generated from the photochemical homolysis of polysilanes



Scheme 1. Postulated Mechanism for Photoreaction of HEMA with phenylsilane.

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.

The polymerization yield of HEMA with 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^[11]. In consideration of the following items: (1) the trend of solubility, polymerization yields, and intrinsic viscosities 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 processes could require high energy, which are anticipated only to occur during the pyrolysis^[12]. However, We should admit at this moment that we can not completely exclude the low degree of cross-linking possibility.

IV Conclusion

This work describes the photopolymerization of HEMA with phenylsilane. While the polymerization yields and intrinsic viscosities of the poly(HEMA)s containing phenylsilyl moieties decreased, the TGA residue yields and intensities of SiH stretching IR bands increased as the molar ratio of phenylsilane over HEMA increased. The phenylsilyl moieties once attached to the poly(HEMA) as an end group, could be left untouched before the pyrolysis

occurring at high temperature. The phenylsilane appeared to competitively and concurrently function as both chain initiation and transfer agents in the polymerization of HEMA.

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