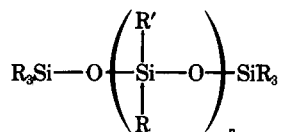


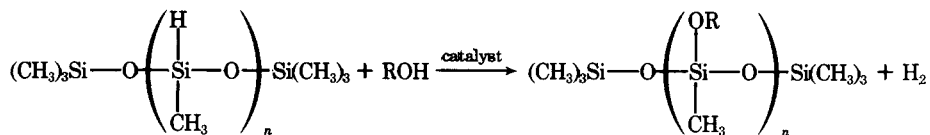
Alcoholysis of Poly(methylhydrogensiloxane)

Silicone liquids are well known as technical materials which are generally composed of linear polyorganosiloxane of the following formula:



Their viscosities are influenced by the degree(n) of polymerization. Organic radicals in commercial silicone liquids usually contain methyl groups and these are often replaced partially by a phenyl group or a hydrogen atom. When R = CH₃ and R' = H, the formula above corresponds to poly(methylhydrogensiloxane) (PMHS), which is prepared by the hydrolysis of methylhydrogendichlorosilane followed by a silanol condensation reaction. PMHS, an excellent water repellent, gels through crosslinking via oxidation or hydrolysis of its hydrogen atom.

It is of interest to synthesize various derivatives of PMHS through the substitution reaction of its labile hydrogen atom. In the present study, reactions between PMHS and various alcohols were attempted to produce new useful silicones. Reaction conditions of the alcoholysis and the gelation behavior of the poly(methylalkoxysiloxane) (PMAS) which resulted are presented herein:



where R = CH₃, C₂H₅, *n*-C₃H₇, *iso*-C₃H₇, *n*-C₄H₉, CH₂CH₂OCH₃, CH₂CH₂OC₂H₅, or C₆H₅; *n* = ≈30.

EXPERIMENTAL

Materials

PMHS used here is a commercial product, Shin-etsu KF 99 silicone liquid (polymerization degree ≈30, specified by supplier). All of the alcohols used were redistilled and dried over anhydrous cupric sulfate or calcium oxide; these were methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, 2-methoxyethanol, 2-ethoxyethanol, and phenol. Inorganic catalysts such as KOH, K₂CO₃, NaOH, Na₂CO₃, Na₂SiO₃, NaHCO₃, Mg(OH)₂, MgCO₃, MgCl₂, Ca(OH)₂, CaCO₃, Ba(OH)₂, BaCO₃, Sr(OH)₂, SrCO₃, CdCl₂, AlCl₃, FeCl₂, FeCl₃, and NiCl₂ were all commercial samples and were used in a powder state or after drying with Abderhalden's apparatus. Amine catalysts such as triethylamine and pyridine were dried over granular KOH after redistillation. Benzene, used as a solvent, was also redistilled and dried over metallic sodium flakes.

Procedure

In order to find suitable reaction conditions, the rate of alcoholysis was semiquantitatively determined by volumetric measurement of evolving hydrogen gas by means of the usual gas buret. The reaction was carried out in a flask which was immersed in a water bath kept at 20° ± 0.3°C under continuous magnetic stirring to ensure uniform treatment. In order to avoid unfavorable side reactions, moisture in the reaction flask was replaced with air before beginning the reaction. The hydrogen evolved was immediately introduced into the gas buret and equilibrated at atmospheric pressure, and readings of the volume were taken. The volume was plotted against time. The rate plot obtained was nearly a straight curve, and in the present work the slope of the curve was regarded as the rate of the reaction. The rate value is only approximate, but nevertheless it can be used in order to compare relative reactivities.

TABLE I
Effect of Types of Catalysts on Evolving Rate of Hydrogen^a

Catalyst in 3 ml CH ₃ OH ^b	Rate, ml/min	Catalyst in 3 ml CH ₃ OH ^b	Rate, ml/min
KOH	— ^c	Ca(OH) ₂	8.33
NaOH	— ^c	NaHCO ₃	4.87
Ba(OH) ₂	474.0	BaCO ₃	3.13
K ₂ CO ₃	373.0	Mg(OH) ₂	1.26
Sr(OH) ₂	50.7	MgCO ₃	1.09
Na ₂ SiO ₃	34.0	MgCl ₂	0.50
Na ₂ CO ₃	26.6	CdCl ₂	0.12
SrCO ₃	16.4	NiCl ₂	0.10
N(C ₂ H ₅) ₃	8.98		

^a Reactants, 0.5 g (8.3 mmole of (CH₃SiHO) units) PMHS, 2.67 g (83 mmole) methanol; solvent, 3 ml benzene; temperature, 20° ± 0.3°C.

^b 20 mole-% Equivalent to the Si-H bond of PMHS used. AlCl₃, FeCl₂, FeCl₃, SrCl₂, CaCl₂, CaCO₃, and pyridine showed no catalytic action.

^c Could not be measured because the gas was evolved too vigorously.

The effect of types of catalysts on the rate of methanolysis was examined. To a 30-ml conical two-neck reaction flask equipped with a magnetic stirrer was added 0.5 g (8.3 mmoles) CH₃SiHO units) PMHS, 2.7 g (83 mmoles) methanol, and 3 ml benzene. The side neck of the reaction flask was connected to the inlet of the gas buret, and 3 ml of a methanol suspension or a solution containing a catalyst of 20 mole % equivalent to Si-H bond of PMHS was added to the reaction mixture by way of a 5-ml syringe inserted in the center neck of the reaction flask. The volume of hydrogen evolved was followed with the gas buret. The results are given in Table I.

The effect of the amount of the catalyst on the rate of methanolysis was examined using triethylamine as a catalyst in the same manner described above. An appropriate amount of triethylamine was added to a solution consisting of 0.5 g PMHS, 0.53 g (16.5 mmoles) methanol, and 2.2 ml benzene. The results are shown in Table II and Figure 1.

The effect of different alcohols on the rate was determined as mentioned above. To a mixed solution of 0.5 g PMHS, 16.5 mmoles of the respective alcohol and 2.2 ml benzene were added in 1.16 ml (0.84 g, 100 mole-% equivalent to Si-H bond of PMHS used) of triethylamine. The results are given in Table III.

Synthesis of Poly(methylalkoxysiloxanes)

A representative workup is described below. To a 100-ml two-necked flask equipped with a reflux condenser, a dropping funnel, and magnetic stirrer were added 25 g methanol and 0.2 g anhydrous potassium carbonate PMHS, 20 g, was added dropwise to the stirred reaction mixture at room temperature while the evolution of hydrogen was controlled. The reaction mixture was treated with a small amount of active carbon, neutralized with ion exchanger (Amberlyst 15), and filtered off. Subsequently, the residual alcohol was completely removed under diminished pressure. Poly(methylmethoxysiloxane) thus isolated was a transparent, colorless, odorless, and viscous liquid. The conclusion of the reaction was recognized by the disappearance of the Si-H band (2175 cm⁻¹) by IR analysis. All PMAS polymers thus prepared were soluble in most organic solvents.

They (PMAS) were characterized as follows: specific gravity was determined with an Ostwald pycnometer, refractive index with an Abbe refractometer, analysis by the digestion method,¹ IR spectrum with a Hitachi 215 grating infrared spectrophotometer, and molecular weight cryoscopically using benzene as the solvent. The results are summarized in Table IV.

Gelation of PMAS

Using the Shimadzu electric melting point measurement apparatus, gelation time was determined at 185°C for 0.3 ml of sample mounted on a glass plate (microslide glass, JIS 1st grade, 76 × 26 × 1 mm). The results are shown in Table V.

TABLE II
Effect of Amount of Catalyst on Rate of Hydrogen Evolution^a

$N(C_2H_5)_3$, mole % ^b	Rate, ml/min
10	0.50
25	0.92
50	1.35
75	1.58
100	1.69
130	1.70
160	1.70
200	1.69

^a Reactants, 0.5 g (8.3 mmole of (CH_3SiHO) units) PMHS, 0.53 g (16 mmole) methanol; solvent, 2.2 ml benzene; temperature, $20^\circ \pm 0.3^\circ C$.

^b Equivalent to the Si—H bond of PMHS used.

IR Spectra of PMHS

It is well known² that the IR absorption band of the Si—H bond of silanes appears at 2100–2300 cm^{-1} . IR measurements of PMHS were carried out using a NaCl plate for liquid film at room temperature. PMHS was used as such and as a 5% solution in triethylamine. The Si—H absorption band appeared at 2175 cm^{-1} and that of the solution, at 2160 cm^{-1} .

RESULTS AND DISCUSSION

In the reaction of PMHS and various alcohols, it was found that among all catalysts tested, basic catalysts except for pyridine exhibit catalytic action, but acidic ones have little or no activity. Pyridine catalyzes the alcoholysis of various monomeric organosilanes³ but does not have an effect on the PMHS system. The cause of this is obscure, though it is perhaps due mainly to the steric effect of PMHS as a polymer.

It is of interest that when triethylamine was used as a catalyst, the rate of methanolysis increased with increasing amount of catalyst until its concentration reached 100 mole % equivalent to Si—H

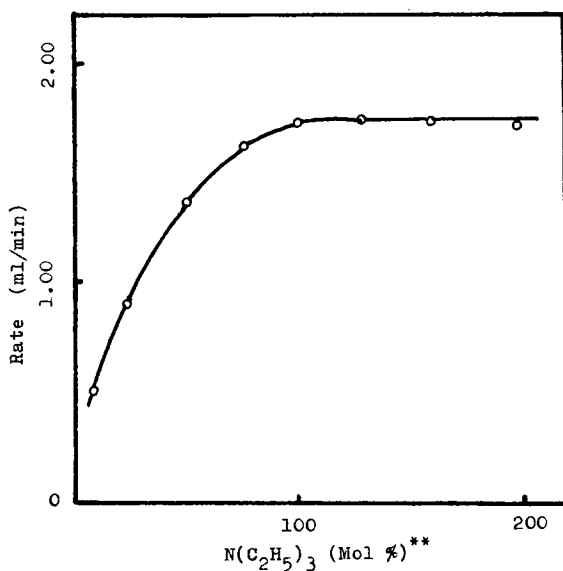


Fig. 1. Effect of amount of catalyst on evolution rate of hydrogen: Reactants, 0.5 g (8.3 mmole of (CH_3SiHO) units) PMHS, 0.53 g (16 mmole) methanol; solvent, 2.2 ml benzene; temperature, $20^\circ \pm 0.3^\circ C$; $N(C_2H_5)_3$ mole-% equivalent to the Si—H bond of PMHS used.

TABLE III
Effect of Kind of Alcohol on Rate of Hydrogen Evolution^a

Alcohol	Rate, ml/min	Alcohol	Rate, ml/min
C ₆ H ₅ OH	2.78	C ₂ H ₅ OH	0.60
CH ₃ OC ₂ H ₄ OH	1.92	<i>n</i> -C ₃ H ₇ OH	0.38
CH ₃ OH	1.57	<i>n</i> -C ₄ H ₉ OH	0.36
C ₂ H ₅ OC ₂ H ₄ OH	1.39	iso-C ₃ H ₇ OH	0.19

^a Reactants, 0.5 g (8.3 mmole of (CH₃SiHO) units) PMHS, 0.53 g (16.5 mmole) methanol; solvent, 2.2 ml benzene; catalyst, triethylamine of 100 mole % equivalent to the Si-H bond of PMHS used; temperature, 20° ± 0.3°C.

TABLE IV.
Syntheses of Poly(methylalkoxysiloxanes)^a

PMHS, ^b g	ROH R	Product (PMAS) yield		Analysis Si, %			Mol. wt		
		g	%	Found	Calcd. ^c				
20	CH ₃	25	27	90	1.171	1.4112	33.86	31.16	6400
20	C ₂ H ₅	35	32	94	1.088	1.4099	29.19	26.96	4600
20	<i>n</i> -C ₃ H ₇	45	39	99	1.032	1.4158	24.85	23.76	5300
20	iso-C ₃ H ₇	45	39	99	1.038	1.4088	26.49	23.76	5100
20	<i>n</i> -C ₄ H ₉	55	43	98	1.040	1.4198	23.65	21.21	5300
20	CH ₃ OC ₂ H ₄	65	43	96	1.172	1.4273	27.80	20.93	6300
20	C ₂ H ₅ OC ₂ H ₄	65	48	97	1.113	1.4287	23.04	18.95	6200
20	C ₆ H ₅	65	50	99	1.187	1.5208	20.32	18.45	6300

^a Catalyst, 0.2 g K₂CO₃.

^b Mol. wt, found value, 2250.

^c Calculated for CH₃Si(OR)O.

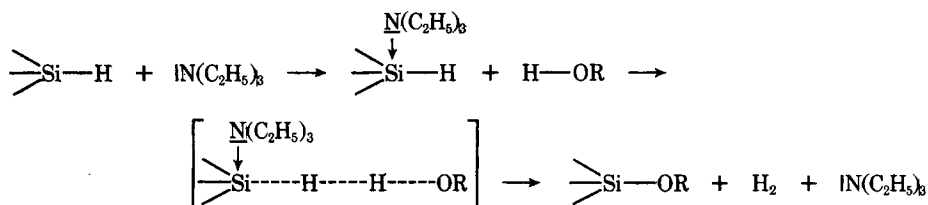
TABLE V
Gelation of Poly(methylalkoxysiloxane)^a

PMAS, RO-	Gel time, min	PMAS, RO-	Gel time, min
CH ₃ O	— ^b	<i>n</i> -C ₄ H ₉ O	120
C ₂ H ₅ O	29	CH ₃ OC ₂ H ₄ O	1
<i>n</i> -C ₃ H ₇ O	120	C ₂ H ₅ OC ₂ H ₄ O	5
iso-C ₃ H ₇ O	120	C ₆ H ₅ O	120

^a Sample, ca. 0.3 ml; temperature, 185°C.

^b Could not be measured as gelation occurred too rapidly.

bond of PMHS. An equilibrium was obtained when the catalyst was further increased beyond 100 mole % (Fig. 1 and Table II). This suggests that triethylamine activates PMHS by coordination to the silicon atom to initiate the reaction of the thus formed intermediate and alcohol. Evidence for this was provided by our finding that the IR spectrum of the Si-H bond of PMHS (2175 cm⁻¹) was shifted toward a lower wave number (2160 cm⁻¹) in a large amount of the amine. This shift may be due to the nucleophilic coordination of the amine to the silicon atom of the Si-H bond. Table III shows the tendency of alcohols possessing an acidic hydrogen atom and a sterically less hindered structure to react more easily than those without these properties. Thus, a possible feature for the formation of PMAS is indicated by the following scheme analogous to the base-catalyzed alcoholysis of triorganosilanes:³



It was found that anhydrous alkali carbonates such as sodium carbonate and potassium carbonate were excellent catalysts for the alcoholysis. Amine catalyst easily controlled the methanolysis but was less favorable because of its lower activity other than methanolysis and ethanolysis.

As shown in Table IV, experimental values of the silicon content of PMAS were always higher than calculated. This means that during treatment, an ether elimination reaction took place to increase $\text{CH}_3\text{SiO}_{3/2}$ units in the PMAS molecule by crosslinking.

PMHS gelled by polycondensation via oxidation or hydrolysis of its hydrogen atom, while the gelation of PMAS seemed to occur through the elimination of ether between alkoxy groups, especially in the absence of moist air. It has been found that alkylalkoxysilanes eliminate ether to give the corresponding siloxanes.⁴ Similar changes may be evident in the PMAS system. PMAS polymers with electronegative alkoxy groups and sterically less hindered alkoxy groups were more easily cured by heating. The gelation of the phenoxysiloxane was relatively slower despite its higher negative phenyl group. The reason for this may be attributed to the steric effect of the bulky phenoxy group.

Poly(methylmethoxysiloxane) was very easily cured by heating without catalysts to give water-repellent film similar to PMHS; it was, therefore, expected to be a new and promising material.

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