Methylhydropolysiloxanes from Cohydrolysis of Methylhydrochlorosilanes and Methylchlorosilanes

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Recently, we reported[1] on the presence of tetramethylsilane (I′) (b. p. 26.5°C), dimethylchlorosilane (II′) (b. p. 36°C), hydrocarbon by-product (b. p. 33°–37°C) and methyldichlorosilane (III′) (b. p. 41°C) in the low boiling product of silicon-methylchloride reaction. We wish now to report on the lower members of copolymer which were obtained by hydrolyzing these two methylhydrochlorosilanes with three kinds of methylchlorosilane.

In this experiment, for the source of $\mathbf{M'}$*, industrial low boiling fraction (b. p. 35°–36°C) was used without further purification. Because of the result of the preceding paper, it was considered to be difficult to obtain pure (II′) by conventional fractionation through an ordinary laboratory column. Also the hydrolyzate of the low boiling fraction used in this experiment was found to be composed of mainly methylhydropolysiloxanes and a small amount of (I′) and the hydrocarbon by-product. The percentage composition of the lower members of the methylhydropolysiloxanes based on the amount of the hydrolyzate is given in Table I (Expt. 1). It was considered that $\mathbf{M'_2}$ was formed from (II′) and the succeeding linear polymers, $\mathbf{M'D'_nM'}$ from (II′) and (III′).

In the preceding paper, a small amount of linear polysiloxanes, $\mathbf{M'DM'}$, $\mathbf{M'D'DM'}$ and $\mathbf{M'D_2M'}$, were found to be present in the hydrolyzate of the low boiling product, but among them only $\mathbf{M'DM'}$ could be characterized. In that case, $\mathbf{D}$ unit was supposed to be formed from (II′) by the fission of Si-H bond during the hydrolysis reaction. In order to obtain sufficient amounts of $\mathbf{M'D'DM'}$ and $\mathbf{M'D_2M'}$, various amounts of dimethyldichlorosilane (II), as a source of $\mathbf{D}$ unit, were added to the low boiling fraction. It succeeded to characterize these two compounds from the hydrolyzate which were obtained by mixing a relatively small amount of (II). The polysiloxane which could be accurately characterized from the cohydrolyzate of trimethylchlorosilane (I) with the low boiling fraction was $\mathbf{MM'}$.

The trisiloxanes which were supposed to be formed, such as $\mathbf{M'DM'}$, $\mathbf{M'D'M}$, $\mathbf{M'DM}$ and $\mathbf{MD'M}$ could not be separated.

Since the linear polysiloxanes were formed from the low boiling fraction itself, it was not easy to separate the branched chain polysiloxanes from the isomeric linear polymers when the low boiling fraction was cohydrolyzed with methyltrichlorosilane (III). Two branched chain polymers, $\mathbf{M'_3T}$ and $\mathbf{M'_2TD'M'}$, could be characterized in this experiment.

Further, a series of copolymer $\mathbf{MD'_nM}$ ($n=1-6$), some of which have already been characterized by Sauer[2], were obtained by cohydrolysis of (I) and (III′).

Properties of copolymers obtained in this experiment are summarized in Table II.

Experimental

Starting Materials.—The low boiling fraction (b. p. 35°–36°C, specific gravity : 0.873, chlorine content: 38.5%) and methylchlorosilanes used in this experiment were supplied from Shin-etsu Chem. Ind. Co. Methyltrichlorosilane and methyldichlorosilane were redistilled through a Stedman column of about 30 theoretical plates and the fraction having the calculated chlorine content was used for the experiments.

Cohydrolysis.—In all cases, cohydrolysis was performed by the same method described in the preceding paper. The fractionation of the hydrolyzate was carried out by a semi-micro Stedman column of about 50 theoretical plates throughout this experiment.

Analysis of Active Hydrogen.—Active hydrogen content was measured by decomposing the sample with aqueous ethanolic sodium hydroxide in a Zerewitinoff's apparatus.

Cohydrolyzate with Dimethyldichlorosilane (II), (Expt. 2–5).—The results of the cohydrolysis are given in Table I. In Expt. 2, 3 and 4, the amounts of (II) mixed were 90, 65 and 51% of the low boiling fraction respectively. In each case, the distribution of the fraction boiling below 150°C was determined. Then the residues of

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1) R. Ōkawara and M. Sakiyama, This Bulletin, 29, 236 (1956).

* In this paper, the shorthand notation will be used which was indicated in the preceding paper[1].

$\mathbf{M'}=H(CH_3)_2SiO_{1/2}$ $\mathbf{M}=(CH_3)_3SiO_{1/2}$
$\mathbf{D'}=HCH_3SiO$ $\mathbf{D}=(CH_3)_2SiO$
$\mathbf{T}=CH_3SiO_{3/2}$

2) R. O. Sauer, W. J. Scheiber and S. D. Brewer, *J. Am. Chem. Soc.*, 68, 962 (1946).

TABLE I

Expt. No.	Mixture of chlorosilanes		Hydrolyzate yield		Composition of the hydrolyzate (%) Disiloxanes			Trisiloxanes			Tetrasiloxanes	Higher siloxanes
		(g.)	(g.)	(%)theory**	$\mathbf{M_2'}$	**MM′**	$\mathbf{M_2}$	**M′D′M′**	**M′DM′**	**MD′M**		
1	(L)*	2200	1120	73	44	—	—	15	1	—	10	19
2	(L) (II)	95 86	86	74	5	—	—	5	17	—	(69)	
3	(L) (II)	113 77	88	71	7	—	—	5	17	—	(68)	
4	(L) (II)	113 58	84	75	10	—	—	7	21	—	(60)	
5	(L) (II)	435 75	250	72	21	—	—	9	19	—	10	28
6	(L) (I)	350 400	390	65	4	24	38	3	(5)		(19)	
7	(L) (III)	380 75	224	75	12	—	—	7	2	—	26	37
8	(III′) (I)	200	345	89	—	—	46	—	—	10	8	30

* (L): The low boiling fraction, (I): $(CH_3)_3SiCl$, (II): $(CH_3)_2SiCl_2$, (III): CH_3SiCl_3, (III′): CH_3SiHCl_2

** Calculated from the chlorine content of the mixture of chlorosilanes.

TABLE II

METHYLHYDROPOLYSILOXANES

Polysiloxanes	Boiling point °C/mmHg ((Reported))2)	Refractive index n_D^{20} Found ((Reported))	Density d_4^{20} Found ((Reported))	Molar refraction Eound (Calcd.)*	Molecular weight Found** (Calcd.)	%H(-Si) Found (Calcd.)
MD′M	141.5/760	1.3818	0.8193	63.18	—	0.45
		((1.3818))	((0.8194))	(63.19)	(222.52)	(0.45)
$\mathbf{MD_2'M}$	81/28	1.3862	0.8556	77.63	—	0.70
		((1.3854))	((0.8559))	(77.46)	(282.66)	(0.71)
$\mathbf{MD_3'M}$	105/28	1.3880	0.8798	91.94	—	0.87
	((85.6/10))	((1.3878))	((0.8806))	(91.73)	(342.79)	(0.88)
$\mathbf{MD_4'M}$	77/2	1.3904	0.8966	106.6	—	1.00
	((107/10))	((1.3895))	((0.8991))	(106.0)	(402.92)	(1.00)
$\mathbf{MD_5'M}$	94/2	1.3920	0.9136	120.7	—	1.08
				(120.3)	(463.06)	(1.09)
$\mathbf{MD_6'M}$	104/2	1.3925	—	—	—	1.11
					(523.19)	(1.16)
MM′	85/760	1.3740	0.7578	44.71	145	0.68
				(44.55)	(148.36)	(0.68)
M′D′DM′	71/26	1.3862	0.8623	73.21	272	1.13
				(73.09)	(268.63)	(1.13)
$\mathbf{M'D_2M'}$	77/25	1.3875	0.8632	77.18	285	0.72
				(77.46)	(282.66)	(0.71)
$\mathbf{M_3'T}$	60/19	1.3852	0.8612	73.13	270	1.14
				(73.09)	(268.63)	(1.13)
$\mathbf{M_2'TD'M'}$	100/38	1.3882	0.8891	87.29	329	1.22
				(87.36)	(328.76)	(1.23)

* Calculated from bond refractivities by E. L. Warrick, *J. Am. Chem. Soc.*, **68**, 2455 (1946).

** Cryoscopic measurements in benzene.

these three runs were gathered and rigorously fractionated. A small plateau (ca. 10 cc.) of **M′D′DM′**, though not so pure (Found: H(−Si), 1.15. Calcd. for **M′D′DM′**: H(−Si), 1.13%.) and a succeeding large plateau (ca. 45 cc.) of gradually rising temperature (80°–85°C/31 mm.) were obtained.

As the refractive index (n_D^{20}) of this incomplete plateau changed from 1.3911 to 1.3935 and the active hydrogen content of the distillate showed a lower value than that of $\mathbf{M'D_2M'}$, it may be natural to suppose that $\mathbf{M'D_2M'}$ was contaminated with cyclic polysiloxanes having **D** (reported[3]: $\mathbf{D_4}$, n_D^{20} 1.3968), or **D** and **D'** units in this plateau.

In Expt. 5, the low boiling fraction was cohydrolyzed with a relatively small amount (17% of the low boiling fraction) of (II) to avoid the formation of cyclic polysiloxanes as far as possible. By redistillation, **M'D'DM'** and $\mathbf{M'D_2M'}$ were obtained as the complete plateaus and were accurately characterized.

Cohydrolyzate with Trimethylchlorosilane (I), (Expt. 6).—The low boiling fraction was cohydrolyzed with (I). The succeeding plateaus of $\mathbf{M'_2}$ (b. p. 70.5°C), **MM'** (b. p. 85°C) and $\mathbf{M_2}$ (b. p. 100°C) were obtained. Above **M'D'M'** (b. p. 117°C), two main plateaus having a gradually changing refractive index were observed until 141°C. One centering around 130°C was supposed to contain a pair of isomers **M'DM'** and **M'D'M** (Found: H(−Si), 0.95. Calcd. for **M'DM'** or **M'D'M**: H(−Si), 0.97%.), the other from 137° to 141°C, **M'DM** and **MD'M** (Found: H(−Si), 0.53. Calcd. for **M'DM** or **MD'M**: H(−Si), 0.45%.). Owing to the close boiling points of isomers in a pair, neither was accurately separated. The distribution of the components in the hydrolyzate is given in Table I.

Cohydrolyzate with Methyltrichlorosilane (III), (Expt. 7).—After $\mathbf{M'D'_2M'}$ has been distilled out, a large plateau (ca. 50 cc.) was obtained between 73°C to 77°C at 38 mm. The first 30 cc. of this plateau had the value of refractive index (n_D^{20}) of 1.3850 to 1.3853 and then it gradually increased to 1.3860. Since the branched chain polysiloxane ($\mathbf{M_3T}$) has been reported[3] to have a slightly lower boiling point and refractive index than the isomeric linear polysiloxane ($\mathbf{MD_2M}$), it was supposed naturally in this experiment that the fore part of this plateau is that of $\mathbf{M'_3T}$ and at the back part of the plateau, $\mathbf{M'_3T}$ is gradually contaminated with accompanying isomeric linear **M'D'DM'** (n_D^{20} 1.3862) which was produced inevitably from the hydrolysis of the starting material. By redistilling the portion having the refractive index 1.3850 to 1.3853, the plateau having the constant refractive index was obtained, and this was assigned to $\mathbf{M'_3T}$.

The succeeding five small plateaus were obtained until 115°C/0.4 mm. Among them only the plateau (100°C/38 mm., n_D^{20} 1.3882), which was found next to the linear $\mathbf{M'D'_3M'}$, had its active hydrogen content and molecular weight consistent with the calculated value for the branched chain pentasiloxane, $\mathbf{M'_2TD'M'}$. But the purity of this compound would not be insisted upon merely because of its hydrogen content and molecular weight, for there is a possibility of contamination of a small amount, if any, of isomeric linear pentasiloxane.

Cohydrolyzate of Methyldichlorosilane (III') and Trimethylchlorosilane (I), (Expt. 8)—A series of methylhydropolysiloxanes indicated by $\mathbf{MD'_nM}$ ($n=1-4$) was first synthesized by Sauer[2], but the boiling points of trisiloxane and tetrasiloxane were not reported. We synthesized a series of these compounds by cohydrolysis of (I) and (III'). As no equilibration by concentrated sulfuric acid was performed to avoid the fission of Si-H by this reagent, trisiloxane was much contaminated with cyclic tetrasiloxane, $\mathbf{D'_4}$ (b.p. 134.5°C) and it was necessary to repeat rigorous fractionation until the distillate gave a satisfactory active hydrogen content. Tetrasiloxane and pentasiloxane were also redistilled once. Octasiloxane was supposed to be not so pure as other compounds referring to its active hydrogen content.

Summary

1) The low boiling fraction of silicon-methylchloride reaction was cohydrolyzed with the three kinds of methylchlorosilane and the methylhydropolysiloxanes, **MM'**, **M'D'DM'**, $\mathbf{M'D_2M'}$, $\mathbf{M'_3T}$ and $\mathbf{M'_2TD'M'}$, have been prepared and characterized.

2) A complete series of linear methylhydropolysiloxanes, $\mathbf{MD'_nM}$ having three to eight silicon atoms have been prepared and characterized from the cohydrolyzate of methyldichlorosilane and trimethylchlorosilane.

We wish to express our hearty thanks to Shin-etsu Chem. Ind. Co. for giving us precious samples.

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[3] W. Patnode and D. Wilcock, *J. Am. Chem. Soc.*, 68, 358 (1946).