Alkylalkoxypolysiloxanes. IV.⁽¹⁾ *Lower Members of Methoxy End-blocked Dimethylpolysiloxanes with One to Six Silicon Atoms*

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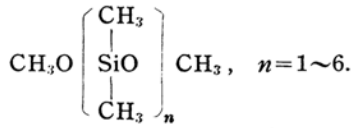
(Received February 16, 1955)

In the preceding paper¹⁾ ethylmethoxypolysiloxanes were synthesized by the condensation reaction of partially methanolyzed ethyltrichlorosilane using sodium bicarbonate. Here, the condensation reaction with sodium bicarbonate has been applied to partially methanolyzed dimethyldichlorosilane, and a series of lower members of methoxy end-blocked dimethylpolysiloxanes has been prepared as indicated below:



$$CH_3O\left(\begin{array}{c}CH_3\\ |\\ SiO\\ |\\ CH_3\end{array}\right)_n CH_3, \quad n=1\sim6.$$

Of these compounds the first member, dimethyldimethoxysilane ($n=1$), was previously obtained by Simpson²⁾ and by Kantor³⁾, but the boiling point only was reported.

Condensation reaction by the use of sodium bicarbonate is shown stoichiometrically in the following expression:

$$(CH_3)_2Si(OCH_3)_xCl_{2-x}+\frac{2-x}{2}NaHCO_3$$

$$\rightarrow (CH_3)_2Si(OCH_3)_xO_{\frac{2-x}{2}}+\frac{2-x}{2}NaCl$$

$$+\frac{2-x}{2}HCl+\frac{2-x}{2}CO_2$$

Just like the ethylmethoxychlorosilane described in the preceding paper¹⁾ this reaction takes place even at room temperature and a slight excess of the amount of sodium bicarbonate calculated from the above formula has been required to produce chlorine-free polysiloxanes.

On fractional distillation of the condensation product, azeotropic mixture of dimethyldimethoxysilane and methanol, a small amount of methanol, and then the lower members of this series were obtained. The distribution of these distillates, varying with the mole ratio (0.9∼1.7) of methanol to dimethyldichlosilane, was plotted against the mole ratios, and the results are shown in Fig. 1. By redistilling these polymers, the presence of a small amount of cyclo-compounds, $[(CH_3)_2SiO]_n$, was found between the succeeding plateaus of the linear compounds from the measurements of refractive index, but the cyclo-compounds have been too small in quantity to be characterized. Physical constants on these linear compounds were determined, and are shown in Table II together with the analytical data.

Experimental

Starting materials. — Dimethyldichlorosilane used in these experiments were supplied from

TABLE I

Exp. No.	Starting Material A $(CH_3)_2SiCl_2$ g. (mole)	 B CH_3OH g. (mole)	 $x=B/A$ (mole ratio)	Dimethylmethoxy-chlorosilane Yield g.	 % theory	Sodium Bicarbonate Calcd. g.	 Added g.	Methoxy End-blocked dimethylpolysiloxane Yield g.	 % theory*
1	64.5 (0.5)	27.0 (0.84)	1.68	52	87	5.6	7.0	40	73
2	64.5 (0.5)	24.0 (0.75)	1.50	53	87	9.1	10.5	39	74
3	65 (0.5)	21.0 (0.66)	1.31	51	83	12.0	13.0	38	74
4	129 (1.0)	38.5 (1.20)	1.20	105	85	28.6	31.0	73	74
5	65 (0.5)	17.5 (0.55)	1.10	54	86	16.8	20.5	37	76
6	65 (0.5)	14.5 (0.45)	0.90	56	88	20.5	22.5	34	72

* Based on the amounts of the starting materials.

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1) Part III of this series, R. Ōkawara, This Bulletin, 28, 360 (1955).

2) P.W. Simpson, Brit. Patent, 635, 726 (April 12, 1950).

3) S.W. Kantor, *J. Am. Chem. Soc.*, 75, 2712 (1953).

the Shin-etsu Chem. Ind. Co. Analysis of hydrolizable chlorine was carried out by hydrolysis in water and titrating the liberated acid. Calcd. for $(CH_3)_2SiCl_2$: Cl, 54.9%. Found: Cl, 54.9%.

Preparation of Methoxy End-blocked Dimethylpolysiloxanes.—Partial methanolysis of dimethyldichlorosilane and the treatment by sodium bicarbonate were carried out as described in the preceding paper[1]. Before the treatment by sodium bicarbonate, the partially methanolyzed product was heated on its refluxing temperature (60°∼65°C) for six to eight hours in order to remove free hydrogen chloride which resulted in the methanolysis.

The amounts of sodium bicarbonate required to obtain the chlorine-free product are given in Table I.

It was found that the yields of the products based on the amount of starting materials were 72∼76%.

Distillation of the Product.—The products obtained in this manner were rigorously fractionated through a semi-micro Stedman column of about 20 theoretical plates. The azeotropic mixture of monomer and methanol was distilled out at first, and methanol which may be formed by the fission of Si-OCH_3, then monomer and dimer fractions, etc., were obtained as the succeeding plateaus. This azeotrope (b.p. 62°C, n_D^{20} 1.3532) was broken with *n*-hexane to give the methanol-*n*-hexane azeotrope (b.p. 49°C). The composition was determined to be 53% dimethyldimethoxysilane and 47% methanol from the above distillation with *n*-hexane and the measurements of refractive index of the mixture of dimethyldimethoxysilane[4] and methanol in various ratios.

The relation between the percentage of each fraction and the mole ratio of the starting materials is shown in Fig. 1.

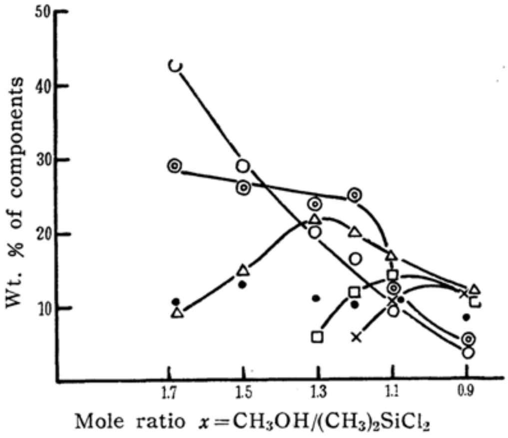

Fig. 1. Composition of the chlorine-free products obtained from sodium bicarbonate treatment.

● Methanol	○ Monomer
◎ Dimer	△ Trimer
□ Tetramer	× Pentamer

Here, the amounts of azeotrope were assigned to each component, and the middle fractions between two plateaus were also assigned to both side fractions.

Monomer[5], dimer and trimer fractions in each run were collected, respectively, and redistilled through the same column. The portions of each plateau having the constant refractive index were

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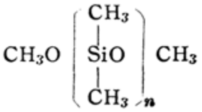
[4] This sample was obtained by the redistillation of monomer fraction, and the data are given in Table II.

[5] Monomer fraction was found in the case of mole ratios 1.2∼1.7.

TABLE II

METHOXY END-BLOCKED DIMETHYLPOLYSILOXANES:



$$CH_3O\left(\begin{array}{c}CH_3\\ | \\ SiO\\ | \\ CH_3\end{array}\right)_n CH_3$$

Polymer Size	Boiling Point °C/mmHg	Density d_4^{20}	Refractive Index n_D^{20}	Molecular Weight Found[b] (Calcd.)	Molar Refraction Found (Calcd.)[c]	% Si Found (Calcd.)
Monomer ($n=1$)	82/760[a]	0.8646	1.3708	— (120.2)	31.51 (31.80)	23.34 (23.36)
Dimer ($n=2$)	139/760	0.9048	1.3835	195 (194.4)	50.17 (50.44)	28.83 (28.90)
Trimer ($n=3$)	83/24	0.9241	1.3892	271 (268.5)	68.67 (69.08)	31.42 (31.38)
Tetramer ($n=4$)	90/5	0.9346	1.3923	345 (342.7)	87.37 (87.72)	32.83 (32.79)
Pentamer ($n=5$)	89/0.5	0.9424	1.3950	415 (416.9)	106.06 (106.36)	33.64 (33.69)
Hexamer ($n=6$)	104/0.5	0.9470	1.3972	484 (491.0)	124.91 (125.00)	34.34 (34.32)
Heptamer ($n=7$)	116/0.5	0.9492	1.4007	— (565.2)	144.57 (143.64)	— —

a) b.p., 81.7°∼82.2°C[2]; 80°∼80.5°C[3].

b) Cryoscopic measurements in benzene.

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

used for the measurements of the physical constants and analysis. Data on these materials are given in Table II.

As the amounts of higher members than tetramer fraction were small in each run, the rigorous separation may not have been attained by the above distillation. Accordingly all of these fractions were collected together, then the distillation was again carried out through a high efficient semi-micro Stedman column (about 60 theoretical plates) as described in the preceding paper[1] and the refractive index was observed throughout the distillation. The results are shown in Fig. 2.

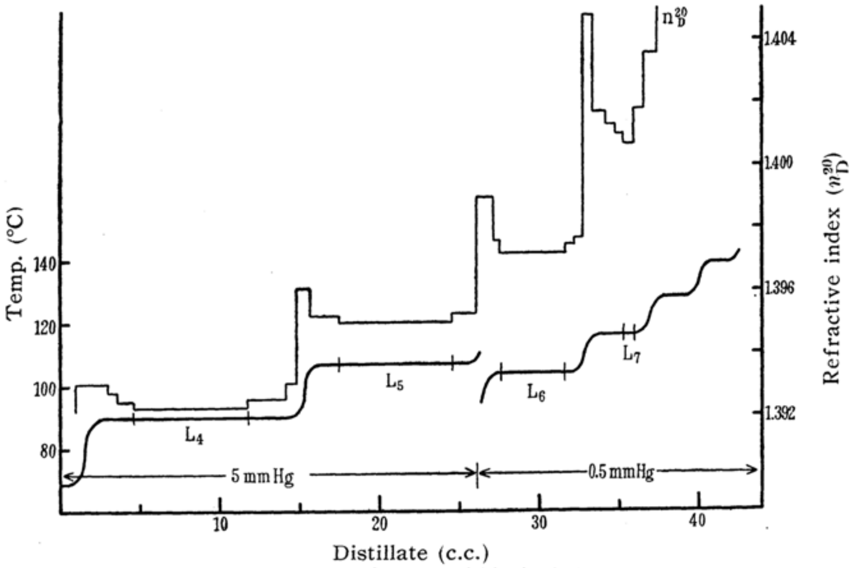


Fig. 2. Distillation curve of methoxy end-blocked dimethylpolysiloxanes. L_n: Linear n-mer

Between the neighbouring plateaus, refractive index higher than that of the both side plateaus was found. From analogy with the preceding paper[1], the presence of the cyclo-compounds may be supposed. Comparing the distillation curve and the refractive index of the distillate in Fig. 2, the plateaus of L_4, L_5 and L_6 were taken as samples. Data on these polymers are also given in Table II. Judging from the refractive index, the members higher than heptamer may not have been separated from cyclo-compounds in this experiment. This fact has been ascertained by comparing the observed and calculated values of the molar refraction for the heptamer as shown in Table II.

Analysis of Silicon.—Silicon in these samples could not be determined by the usual digestion method with concentrated sulfuric acid, so the method using a gelatine capsule with concentrated sulfuric acid was developed. The analytical procedure, which will be soon published in detail, is as follows: 0.2 to 0.5 g. of sample weighed in a size 0 or 1 gelatine capsule was placed in a platinum crucible and the full amount of concentrated sulfuric acid to cover the capsule was added. At this time, the capsule floating on the sulfuric acid was pushed to the bottom of the platinum crucible by pressing it down with a glass rod, and it was left alone there at the room temperature. After two or three hours, the sulfuric acid decomposed the gelatine capsule and was mixed with the sample. This mixture in the covered crucible was heated with a small flame until a brown color appeared, then the acid was evaporated and the carbon was burned off using a low flame. The white residue was then ignited and weighed as silica.

Summary

(1) Methoxy end-blocked dimethylpolysiloxanes have been prepared by the reaction of sodium bicarbonate with partially methanolyzed dimethyldichlorosilane.

(2) Distribution of the lower polymers was determined in regard to the composition of the partially methanolyzed dimethyldichlorosilane.

(3) Methoxy end-blocked dimethylpolysiloxanes from monomer (dimethyldimethoxysilane) to hexamer have been characterized.

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