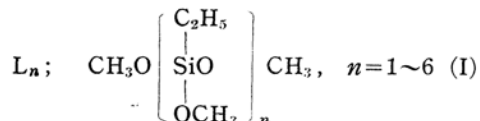


Alkylalkoxypolysiloxanes. III.¹⁾ Lower Members of Ethylmethoxypolysiloxanes with One to Six Silicon Atoms

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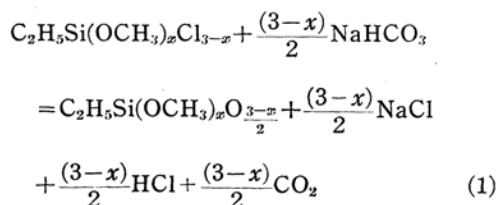
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In the preceding papers, ethylethoxypolysiloxanes²⁾ and ethylisopropoxypolysiloxanes¹⁾ have been prepared and characterized. This paper will describe a series of lower members of linear ethylmethoxypolysiloxanes as indicated by formula (I).



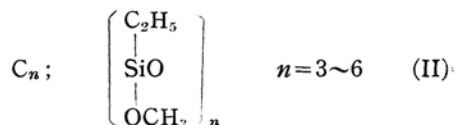
As already described, the partially alcoholized ethyltrichlorosilane was easily polymerized by refluxing, liberating ethylalkoxypolysiloxanes. Thus ethylethoxy- and ethylisopropoxy- polysiloxanes have been prepared.

On the other hand, however, when the mixture of ethyltrichlorosilane and methanol in various mole ratios (1.6-2.5) was refluxed, the thermal reaction occurred with difficulty on prolonged refluxing. It was found that by the addition of sodium bicarbonate the condensation reaction occurred easily by evolving hydrogen chloride and carbon dioxide to the formation of polysiloxanes of the various polymer sizes.



This reaction takes place even at room temperature until the mixture becomes chlorine-free and a slight excess of sodium bicarbonate calculated from the above formula has been required to produce chlorine-free polysiloxanes. Furthermore, the chlorine-free product, such as ethyltrimethoxysilane, does not easily react with sodium bicarbonate in a short period of time even at the refluxing temperature.

On fractional distillation, a small amount of methanol and the lower members of the series (I) (L_n) were obtained. The amounts of these polymers were varied with the chlorine content of the mixture. The distribution of the lower members of series (I) was plotted against the mole ratios x of methanol to ethyltrichlorosilane, and the results are shown in Fig. 1. By redistilling these polymers, the presence of a small amount of cyclocompounds of the series (II) (C_n) was also found between the succeeding plateaus of the linear polymers (L_n),



but they could not be accurately characterized. Analysis and physical properties of the linear polymers are given in Table II.

Experimental

Starting Materials.—The ethyltrichlorosilane used in this experiment was prepared by the reaction of ethylchloride with copper-silicon and was purified by fractionation through a helices-

1) Part II of this series, R. Okawara and I. Ishimaru, This Bulletin, 27, 582 (1954).

2) R. Okawara, This Bulletin, 27, 428 (1954).

packed column of about 20 plates. The redistilled fraction having the boiling point 98°–99°C/760 mm Hg was taken as a starting material. Analysis of hydrolyzable chlorine was carried out by hydrolysis in water and titrating the liberated acid.

Anal. Calcd. for $C_2H_5SiCl_3$: Cl, 65.0 Found: Cl, 64.0.

Preparation of Ethylmethoxypolysiloxanes

(a) **Partial Methanolysis.**—Ethyltrichlorosilane was placed in a 300 cc. three-necked flask equipped with an efficient stirrer, a dropping funnel and a reflux condenser and was cooled with an ice bath. Methanol was added drop by drop with vigorous stirring. After the addition the temperature of the mixture was gradually raised to 40°–50°C. Then the mixture was replaced in a 100 cc. flask equipped with a reflux condenser and heated gradually to its boiling point. The constant refluxing mixture was obtained. The refluxing temperature and the weight of the mixture scarcely changed even after refluxing 30 hours. In this experiment, the constant refluxing mixture was heated on its refluxing temperature for a few additional hours in order to completely remove any trace of free hydrogen chloride which resulted in the methanolysis. The yield and the refluxing temperature were slightly different according to its composition as shown in Table I.

mixture sodium bicarbonate was added. Hydrogen chloride may also be produced by the reaction, so it is desirable that sodium bicarbonate is added differentially to partially methanolized product and the free hydrogen chloride formed is removed successively from the reaction system. Since sodium bicarbonate powder causes a violent reaction even at room temperature, 1–2 g. of sodium bicarbonate powder, or more conveniently tableted powder, was added differentially to the ethylmethoxychlorosilane at room temperature and the mixture was gradually heated to its refluxing temperature in order to expel the free hydrogen chloride after carbon dioxide had ceased to evolve. Then the mixture was cooled to room temperature and the same treatment was repeated until the fuming chlorine compound could not be detected in the mixture. The sodium chloride formed was filtered off and the filtrate was again tested with the Beilstein test to assure that no trace of chlorine compound was present in the mixture.

The amounts of bicarbonate required to produce chlorine-free mixture are given in Table I. It was found that the yields of the polymer based on the amount of the starting materials were 75–85%.

To test whether the ethylmethoxypolysiloxanes react with sodium bicarbonate or not, redistilled ethyltrimethoxysilane (21 g.) mixed with powdered

TABLE I
RESULTS OF THE SODIUM BICARBONATE TREATMENT

Exp.	Starting Materials			Ethylmethoxychlorosilane	Sodium Bicarbonate		Ethylmethoxypolysiloxane			
	A	B	$x = B/A$	Refluxing Temp.	Yield		Added	Calcd.	Yield	
	$C_2H_5SiCl_3$	CH_3OH			g.	%theory			g.	%theory*
	g. (mole)	g. (mole)	(mole ratio)	°C	g.	%theory	g.	g.	g.	%theory*
1	54.5 (0.333)	27 (0.85)	2.54	123	47	92	7.3	6.0	39.5	85
2	54.5 (0.333)	24 (0.75)	2.25	119	47	92	12.3	9.7	34.0	77
3	81.7 (0.5)	30.5 (0.95)	1.9	118	73	94	27.0	21.8	48.5	78
4	81.7 (0.5)	29 (0.9)	1.82	116	75	96	26.5	24.0	48.0	78
5	81.7 (0.5)	25.6 (0.8)	1.6	115	74	95	30.1	27.8	44.0	75

* Based on the amount of the starting materials.

When an incompletely dehydrochlorinated mixture was used, the free hydrogen chloride which remained in the methanolysis product reacted with sodium bicarbonate added in the following step to liberate water, and the condensation reaction resulted in the formation of the highly polymerized product.

(b) **Reaction of the Partial Methanolysis Product with Sodium Bicarbonate.**—To this

sodium bicarbonate (5 g.) was refluxed for 10 hours. The filtrate (16 g.) was composed of methanol (1 g.), unreacted ethyltrimethoxysilane (12 g.) and the residue (3 g.). This reaction did not proceed smoothly, but with violent bumping.

Distillation of the Polymer.—The polymer thus formed was rigorously fractionated through a semi-micro Stedman column of about 20 theoretical plates. Methanol which may be formed

by the fission of Si-OCH_3 in the bicarbonate treatment, distilled out at first; and then monomer, dimer, trimer and tetramer fractions were obtained as the succeeding plateaus. The relation between the percentage composition of these fractions and the composition of the starting materials are shown in Fig. 1.

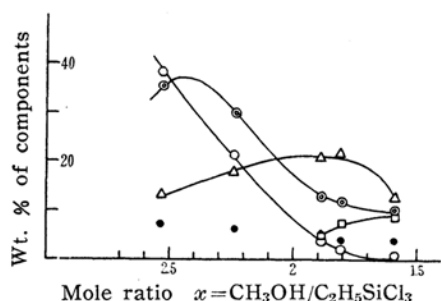


Fig. 1. Composition of the chlorine-free products obtained from sodium bicarbonate treatment.

● Methanol, ○ Monomer,
⊙ Dimer, △ Trimer,
□ Tetramer.

Monomer, dimer and trimer fractions were redistilled through the same column and the refractive index was observed throughout the distillation. The middle portion of the plateau having the constant refractive index was taken for the sample. Data on these polymers are given in Table II.

Between the plateaus of dimer and linear trimer, at the boiling point of $69^\circ\text{C}/0.5\text{ mm Hg}$, a knick point on the distillation curve was found

and the higher refractive index (n_D^{20} 1.4100) at this point than the other portions was also found. From analogy with the preceding papers, the presence of the cyclotrimer may be supposed at this point, but as the amount of this portion was very small, the rigorous separation could not be attained.

As the amount of the tetramer fraction was small in each experiment, the residues of each experiment of Table I and the similar several runs (120 g.) were simply distilled and the fraction distilled out under $200^\circ\text{C}/0.3\text{ mm Hg}$ was collected (80 g.). Since the still temperature was not over 240°C it may be supposed that the thermal rearrangement of the polysiloxane³⁾, which has been reported to begin at above 350°C , did not occur. This distillate was rigorously fractionated through the same semi-micro Stedman column. It was found from the silicon content that the separation of cyclotetramer and linear tetramer was fairly good, but with the polymer higher than this, the rigorous separation could not be attained.

To attain the rigorous separation, the distillation was again carried out through a high efficient semi-micro Stedman column (packed length 54 cm., inner diameter 1.1 cm., 60 theoretical plates, hold-up 3 cc. and pressure drop 2 mm Hg at the total reflux rate of 80 cc./hour). The results with regard to the polymers except monomer and dimer are shown in Fig. 2.

Comparing the distillation curve and the refrac-

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

TABLE II

<div> <div>ETHYLMETHOXYPOLYSILOXANES: CH₃O</div> <div> <div>C₂H₅</div> <div>SiO</div> <div>OCH₃</div> </div> <div>CH₃</div> </div> <div> <div></div> <div>n</div> </div>						
Polymer Size	Boiling Point °C/mm Hg	Density d_4^{20}	Refractive Index n_D^{20}	Molar Refraction Found (Calcd.)**	Molecular Weight Found*** (Calcd.)	% Si Found (Calcd.)
Series I; L _n						
Monomer* (<i>n</i> =1)	124.3/760	0.9488	1.3838	37.02 (37.19)	— (150.3)	18.66 (18.69)
Dimer (<i>n</i> =2)	97/20	1.0071	1.3979	60.95 (61.22)	252 (254.4)	22.05 (22.08)
Trimer (<i>n</i> =3)	90/0.5	1.0335	1.4045	84.93 (85.25)	359 (358.6)	23.48 (23.50)
Tetramer (<i>n</i> =4)	125/0.3	1.0499	1.4094	109.07 (109.28)	462 (462.8)	24.29 (24.28)
Pentamer (<i>n</i> =5)	150/0.3	1.0621	1.4140	133.40 (133.31)	554 (567.0)	24.79 (24.77)
Hexamer (<i>n</i> =6)	170/0.3	1.0744	1.4180	157.43 (157.34)	— (671.2)	25.29 (25.11)

* A. Ladenburg, *Ann.*, **173**, 143 (1874); *Ber.*, **5**, 1081 (1872) b.p. $126/760$, d_4^{20} 0.9747.

J. Emeleus and S. R. Robinson, *J. Chem. Soc.*, **1947** 1592 b.p. 123.

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

*** Cryoscopic measurements in benzene.

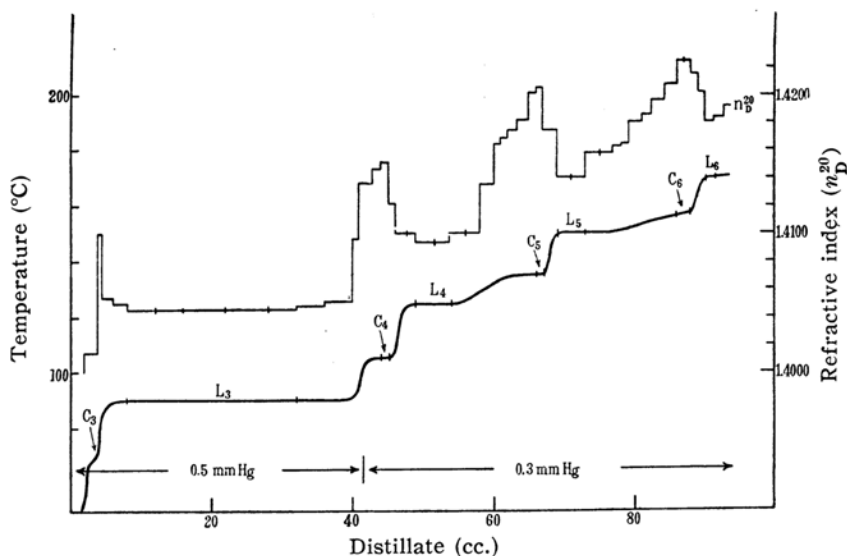


Fig. 2. Distillation curve of ethylmethoxypolysiloxanes.
 L_n : Linear n -mer, C_n : Cyclo- n -mer

tive index of the distillate in Fig. 2, the plateaus of L_3 , C_4 , L_4 , C_5 , L_5 , C_6 and L_6 were taken for the sample.

From the analytical data of C_4^* and C_5^* and from the analogy of a preceding paper¹⁾, it was supposed that C_n is the cyclocompound as indicated by formula (II), but the amount of these cyclocompounds is not enough to separate them from the neighbouring linear compounds. It was found in Fig. 2, that between the plateaus of linear trimer (L_3) and linear tetramer (L_4) there had appeared a plateau of cyclotetramer (C_4), having a higher refractive index than L_3 and L_4 and having a boiling point closer to L_3 than L_4 . The similar relations may be seen with the other cyclocompounds.

Analysis of Silicon.—Monomer was weighed in gelatine capsule, the higher polymer were weighed in a platinum crucible and decomposed by concentrated sulfuric acid.

* Anal. Calcd. for C_4 : Si, 26.96%. Found: Si, 25.31%.
 Anal. Calcd. for C_5 (mol. wt. 521): Si, 26.96%.
 Found: Si, 25.92% (mol. wt. 490, in benzene).

Summary

(1) Ethylmethoxypolysiloxanes have been prepared by the reaction of sodium bicarbonate with partially methanolized ethyltrichlorosilane.

(2) Distribution of the lower polymers was determined with regard to the composition of the partially methanolized product.

(3) Linear ethylmethoxypolysiloxanes containing from one to six silicon atoms have been prepared and characterized.

(4) Ethylmethoxycyclopolsiloxanes containing from three to six silicon atoms have been found, but they could not be accurately characterized.

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