Alkylalkoxypolysiloxanes. I. Ethylethoxypolysiloxanes

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A series of ethylethoxypolysiloxanes as indicated by formula I and a somewhat similar series[1] were prepared by hydrolyzing the corresponding alkyltriethoxysilane, but the products were not accurately characterized.

$$C_2H_5O\left(\begin{array}{c}C_2H_5\\|\\SiO\\|\\OC_2H_5\end{array}\right)_n C_2H_5 \qquad \text{I}$$

The methylethoxypolysiloxanes[2], having the similar structure as the series I, have also been prepared by the partial hydrolysis of methyltriethoxysilane.

This paper will describe a series of lower members (n=1~4) of ethylethoxypolysiloxanes (series I) which were prepared by a thermal reaction between ethylethoxychlorosilanes and ethyltriethoxysilane at the refluxing temperature.

The thermal reaction between ethyldiethoxychlorosilane and ethyltriethoxysilane was found in the quantitative study of partial ethanolysis of ethyltrichlorosilane to determine the ratio of reaction rate of this competitive consecutive reaction[3]. For the purpose of characterizing these polymerized products, pure ethyldiethoxychlorosilanes and ethyltriethoxysilane were mixed in various mol ratios and refluxed. Changings of the weight, the chlorine content and the boiling point of the mixture were pursued through the reaction. When the chlorine content of the mixture was reduced practically to zero, the mixture was fractionated. A series of linear polymers (series I) was obtained. The first plateau was unreacted ethyltriethoxysilane and subsequent plateaus were the succeeding members of this series. By redistilling these polymers, the presence of a small amount of cyclo-compounds, probably cyclotrimer and cyclotetramer, were found between the succeeding plateaus of linear polymers, but owing to the small amount these cyclo-compounds could not be characterized. Analysis and physical properties of the linear polymers are given in Table II. Properties of the ethyltriethoxysilane are also included for the purpose of comparison.

This thermal reaction was not limited in the case of ethylethoxypolysiloxanes, but the case of ethyl isopropoxy-, ethylmethoxy-, and methylmethoxy-polysiloxanes will soon be reported.

Experimental

Starting Materials.—The ethylethoxychlorosilanes and ethyltriethoxysilane used in this experiment were prepared by the partial ethanolysis of ethyltrichlorosilane[3]. The partial ethanolysis products were fractionated twice through a stedman column of about 20 theoretical plates. Ethylethoxydichlorosilane, ethyldiethoxychlorosilane and ethyltriethoxysilane thus obtained have the following properties.

Ethylethoxydichlorosilane: b.p. 66°C/100 mm Hg, n_D^{20} 1.4100, d_4^{20} 1.0876. Anal. Calcd. for $C_2H_5Si(OC_2H_5)Cl_2$: Cl, 41.0. Found: Cl, 40.4%.

Ethyldiethoxychlorosilane: b.p. 85°C/85 mm Hg, n_D^{20} 1.4007, d_4^{20} 0.9793. Anal. Calcd. for $C_2H_5Si(OC_2H_5)_2Cl$: Cl, 19.4. Found; Cl, 19.1%.

Ethyltriethoxysilane: b.p. 61°C/14 mmHg, n_D^{20} 1.3911, d_4^{20} 0.8963. Anal. Calcd. for $C_2H_5Si(OC_2H_5)_3$: Si, 14.57. Found: Si, 14.50%.

A. Thermal Reaction of Ethyltriethoxysilane and Ethylethoxychlorosilanes: Preparation of the Compounds of the Series I.—Ethylethoxychlorosilane and ethyltriethoxysilane were mixed as shown in Table I. By refluxing, the weight of the mixture and the chlorine content were gradually decreased. After the chlorine content of the mixture practically disappeared, the mixture was further refluxed and tested with Beilstein test to assure that no trace of chlorine compound was found in it. The time needed to produce chlorine free mixture and the highest refluxing temperature attained are cited in Table I.

The products were fractionated through a semimicro stedman column of about 30 theoretical plates under reduced pressure. Unreacted ethyltriethoxysilane was distilled out between 66°–76° C/22–30 mmHg. The disiloxane and trisiloxane fractions were the succeeding plateaus which were obtained at 64°–66° C/0.8 mmHg and 101°–6° C/0.8 mmHg. The amounts in percentage of these plateaus including the intermediate fractions cut on the distillation curve are also shown in Table I.

B. Redistillation of the Polysiloxanes. Isolation and Characterization of Linear Poly-

1) K. Andrianov, *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1255 (1938); **16**, 939 (1946).
2) H. J. Fletcher and M. J. Hunter, *J. Am. Chem. Soc.*, **71**, 2922 (1946).
3) R. Okawara, S. Numa and T. Watase, *J. Chem. Soc. Japan, Ind. Sec.* **57**, 118 (1954) (in Japanese).

TABLE I
RESULTS OF THE THERMAL REACTION

Exp. No.	Starting Material: Compound	(g)	(mol.)	Reaction: Time (hr)	Temp. (°C)	Product: (g)	(%theory)	Polysiloxane Fraction: Monomer (%)	Dimer (%)	Trimer (%)	Residue (%)
1	$C_2H_5Si(OC_2H_5)_2Cl$	11	0.06	45	189	17	90	17	31	22	30
	$C_2H_5Si(OC_2H_5)_3$	11.6	0.06								
2	$C_2H_5Si(OC_2H_5)Cl_2$	8.6	0.05	45	192	20	82	13	10	16	61
	$C_2H_5Si(OC_2H_5)_3$	19.2	0.1								
3	$C_2H_5Si(OC_2H_5)_2Cl$	18.5	0.1	47	212	19.5	91	13	27	27	33
	$C_2H_5Si(OC_2H_5)_3$	9.6	0.05								
4	$C_2H_5Si(OC_2H_5)Cl_2$	9	0.05	62	192	26	88	19	19	29	33
	$C_2H_5Si(OC_2H_5)_3$	24	0.12								

TABLE II
ETHYLETHOXYPOLYSILOXANES

Polymer size	Name	Formula	Boiling Point °C/mm	Density d_4^{20}	Refractive Index n_D^{20}	Molar Refraction Found (Calcd.)*	Molecular Weight Found** (Calcd.)	%Si Found (Calcd.)	%C Found (Calcd.)	%H Found (Calcd.)
Monomer	Triethoxyethylsilane	$C_2H_5O(SiO(OC_2H_5)_2)_1C_2H_5$	61/14	0.8963	1.3911	50.98 (51.08)	—	14.50 (14.57)	—	—
Dimer	Tetraethoxy-1, 3-diethyldisiloxane	— ( )$_2$ —	65/0.8	0.9473	1.4006	79.53 (79.74)	315 (310)	18.12 (18.06)	46.26 (46.49)	9.44 (9.68)
Trimer	Pentaethoxy-1, 3, 5-triethyltrisiloxane	— ( )$_3$ —	101/0.8	0.9750	1.4074	108.4 (108.4)	435 (429)	19.70 (19.64)	44.83 (44.82)	9.39 (9.34)
Tetramer	Hexaethoxy-1, 3, 5, 7-tetraethyltetrasiloxane	— ( )$_4$ —	122/0.8	0.9960	1.4148	137.2 (137.0)	556 (546)	20.63 (20.64)	44.20 (43.92)	8.93 (9.17)

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

** Cryoscopic measurements in benzene

mers of Series I.—As the amounts of disiloxane and trisiloxane fraction were small in each experiment, all the polysiloxane fractions except monosilane fraction were gathered (55g.) and again fractionated rigorously through the same column. The distillation curve and the refractive index of the small portions are shown in Fig. I.

The plateaus A, B and C in Fig. I were found to be dimer (tetraethoxy-1, 3-diethyldisiloxane), linear trimer (pentaethoxy-1,3,5-triethyltrisiloxane) and linear tetramer (hexaethoxy-1, 3, 5, 7-tetraethyltetrasiloxane) respectively. Properties of these compounds are given in Table II.

From the knick point of the distillation curve between A and B, and the high refractive index at this portion, the presence of a compound was supposed at this point, but owing to the small amount this compound could not be isolated. Appearance of cyclotrimer (triethoxy-1, 3, 5-triethylcyclotrisiloxane) may be probable at this point, for in the analogous case of ethylisopropoxypolysiloxanes prepared by the same method, the cyclotrimer, which was isolated and characterized, was found

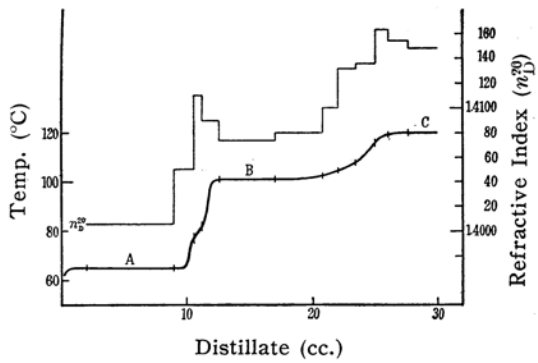

Fig. I. Redistillation curve of ethylethoxypolysiloxanes and the refractive index of the distillates.

A: Dimer
B: Linear trimer
C: Linear tetramer

to be distilled out between the plateaus of dimer and linear trimer. The high refractive index which was found between B and C may also seem to be caused by the presence of cyclo-compound, probably cyclotetramer.

C. Analysis of Silicon.—Silicon was determined by decomposing the sample with concentrated sulfuric acid.

Summary

(1) Ethylethoxypolysiloxanes have been prepared by a thermal reaction of ethylethoxychlorosilanes and ethyltriethoxysilane.

(2) Linear ethylethoxypolysiloxanes containing from 2 to 4 silicon atoms have been prepared and characterized.

(3) Certainly, a small amount of ethylethoxycyclopolysiloxanes were formed by the thermal reaction but they could not be isolated.

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