Alkylalkoxypolysiloxanes. V.[1] *Lower Members of Vinylmethoxypolysiloxanes with One to Five Silicon Atoms*

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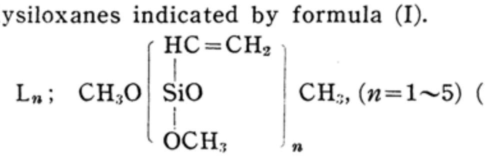
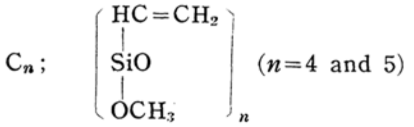
Recently, some data on vinylalkoxy-silanes and -disiloxanes[2] were presented, but no data on higher vinylalkoxypolysiloxanes have been reported. We wish now to report on the preparation and properties of vinylmethoxypolysiloxanes indicated by formula (I).


$$L_n;\ CH_3O\left[\begin{array}{c}HC=CH_2\\ |\\ SiO\\ |\\ OCH_3\end{array}\right]_n CH_3,\ (n=1\sim5)\quad (I)$$

For the preparation of the polymers, the method was used which is similar to that in the case of preparing ethylmethoxypolysiloxanes[3] and methoxy end-blocked dimethylpolysiloxanes.[1] Sodium bicarbonate was added to the partially methanolyzed vinyltrichlorosilane, which was prepared by mixing 1 mole of vinyltrichlorosilane and x moles (x=1.6-2.6) of methanol. The liberated chlorine-free product was fractionated at as low a temperature as possible under reduced pressure to avoid the thermal polymerization of vinyl radical. A small amount of methanol was distilled out at first; then the lower members of the series (I) were obtained. The percentage composition of the lower members were plotted against the mole ratios x, and the results are shown in Fig. 1.

Monomer and dimer fractions were redistilled, respectively. The higher polymers were obtained from the residue of each experiment. To avoid the polymerization, the residue was rapidly distilled out at a pressure of 1 mm Hg until the stil-pot temperature reaches 220°C. The distillate thus obtained was rigorously fractionated through a high efficient column. Properties of the linear polymer are given in Table II. During the course of this fractionation, a long peroid of heating at high temperature (until 200°C/1 mm Hg) were required, but any polymeric changes such as gellation were not observed. The appearance of cyclo-compounds as indicated by formula (II) were also observed between the plateaus of the linear compounds, as in the case of preceding papers [1,3] but they could not be accurately characterized.


$$C_n;\ \left[\begin{array}{c}HC=CH_2\\ |\\ SiO\\ |\\ OCH_3\end{array}\right]_n\ (n=4\text{ and }5)\quad (II)$$

Experimental

Starting Material.—Vinyltrichlorosilane was presented from Linde Air Products Company.

Preparation of Vinylmethoxypolysiloxanes

(a) Partial Methanolysis and Polymerization with Sodium Bicarbonate.—In this experiment, a procedure similar to that already described[1),3)] was used. To complete the reaction,

TABLE I

	Starting Material			Vinylmethoxychlorosilane				Sodium Bicarbonate		Vinylmethoxypolysiloxane	
	A	B		Refluxing Temp.	Cl	Yield		Added	Calcd*.	Yield	
	$CH_2=CHSiCl_3$	CH_3OH	x=B/A			Found	% theory			Found	% theory**
	g.	g.	mole ratio	°C	%	g.	%	g.	g.	g.	%
1	40.4	20.9	2.6	122	4.5	35.5	94.7	2.7	2.5	28.5	82
2	40.4	18.4	2.3	122	12.3	35.0	92.5	5.5	5.0	27.0	82
3	80.8	32.0	2.0	122	20.0	70.0	91.7	17.8	17.5	45.0	73
4	40.4	15.2	1.9	123	16.0	34.0	88.8	7.9	7.4	21.0	68
5	80.8	28.8	1.8	121	23.5	71.0	92.4	20.0	19.5	43.0	71
6	40.4	12.8	1.6	120	22.0	34.0	88.1	10.5	10.0	12.0	42

* 1 Mol. of sodium bicarbonate was assumed to be equivalent to 2 g.-atoms of Cl contained in the chlorosilane mixture.

** Based on the amount of the starting materials.

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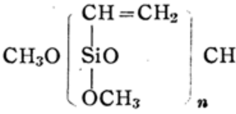
[1] Part IV of this series, T. Tanaka and R. Ōkawara, This Bulletin, 28, 364 (1955).

[2] R. Nagel and H.W. Post, *J. Org. Chem.*, 17, 1382 (1952); R. Nagel, C. Tamborski and H.W. Post, ibid., 16, 1768 (1951).

[3] R. Ōkawara, This Bulletin, 28, 360 (1955).

TABLE II

VINYLMETHOXYPOLYSILOXANES:



$$CH_3O\left(\begin{array}{c} CH{=}CH_2 \\ | \\ SiO \\ | \\ OCH_3 \end{array}\right)_n CH_3$$

Polymer Size	Boiling Point °C/mm Hg	Density d_4^{20}	Refractive Index n_D^{20}	Molecular Weiget Found* (Calcd.)	Molar Refraction Found (Calcd.)**	% Si Found (Calcd.)
Monomer	122/760	0.9700	1.3930	—	36.48	18.85
($n=1$)[a]				(148.24)	(36.72)	(18.95)
Dimer	86/11	1.0361	1.4107	248	59.97	22.55
($n=2$)[b]				(250.40)	(60.28)	(22.44)
Trimer	81/0.8	1.0636	1.4192	354	83.74	23.94
($n=3$)				(352.57)	(83.84)	(23.90)
Tetramer	109/0.3	1.0784	1.4230	448	107.36	24.67
($n=4$)				(454.73)	(107.40)	(24.71)
Pentamer	135/0.3	—	1.4284	—	—	24.94
($n=5$)				(556.91)	(130.96)	(25.22)

a) R. Nagel, C. Tamborski and H. W. Post, loc. cit b.p. 52.9/46, 59.5/62, d_4^{25} 0.9669, n_D^{25} 1.3910 and MR_D 36.42.

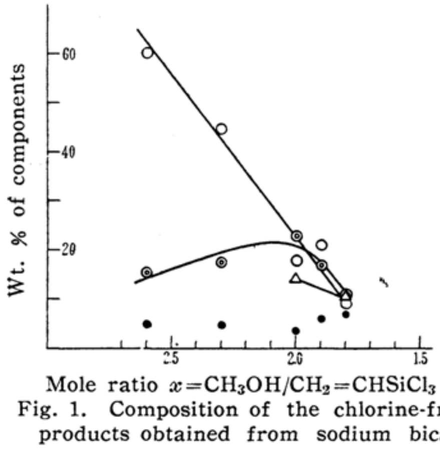
b) R. Nagel, C. Tamborski and H. W. Post, ibid. b.p. 120–20.6/46, d_4^{25} 1.0627, n_D^{25} 1.4172 and MR_D 59.28.

* Cryoscopic measurements in benzene.

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

the partially methanolyzed product was refluxed for 8–10 hours. The results are summarized in Table I.

The distribution of the lower polymers in the product was determined by fractionation through a semi-micro Stedman column of about 30 theoretical plates. The results are shown in Fig. 1.



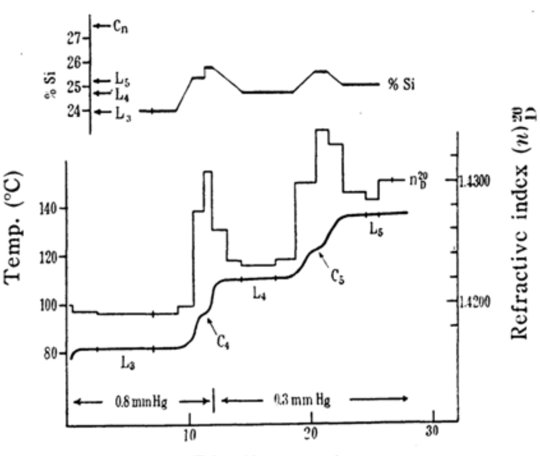
Mole ratio $x=CH_3OH/CH_2{=}CHSiCl_3$

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

● Methanol, ○ Monomer,
◎ Dimer, △ Trimer.

The product of Exp. 6 was a slightly viscous liquid and the composition could not be determined by fractionation, because the gellation occurred at 180°C/15 mm Hg in the stil-pot.

(b) Redistillation of the Polysiloxanes.— Monomer and dimer fractions were redistilled through the same column and the portions having the constant boiling point and refractive index were analyzed. The residues of Exp. 1–5 were simply distilled by a Claisen flask under 1 mm Hg until the stil-pot temperature reaches 220°C. The product distilled out below 170°C (40 g.) was fractionated rigorously through a high efficient semi-micro Stedman column of about 60 theoretical plates. The refractive index and the silicon content of the distillate are shown in Fig. 2.



Distillate (cc.)

Fig. 2. Distillation curve of vinylmethoxypolysiloxanes.

L_n: Linear n-mer,
C_n: Cyclo-n-mer

The plateaus L_3, L_4 and L_5 were those of linear trimer, tetramer and pentamer, respectively. Between these plateaus the portions, C_4 and C_5, having a higher refractive index and a higher silicon content than the neighbouring portions were found.

From the silicon content and from the analogy of the preceding papers, C_4 and C_5 may be seen to be impure cyclotetramer and cyclopentamer respectively, indicated by formula (II). A slightly higher value of refractive index in front of the plateau of linear trimer was found in this experiment, but it may not be enough to suppose the presence of cyclotrimer.

Analysis of Silicon.—Monomer and dimer were weighed in gelatine capsule[1]; the higher polymers were weighed in a platinum crucible and decomposed by concentrated sulfuric acid.

Summary

(1) Vinylmethoxypolysiloxanes have been prepared by the reaction of sodium bicarbonate with partially methanolyzed vinyltrichlorosilane.

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

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

(4) Vinylmethoxycyclopolysiloxanes were found between the plateaus of linear polymer but they could not be accurately characterized.

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