Alkylalkoxypolysiloxanes. VII.[1] *Lower Members of tert-Butoxy End-blocked Dimethylpolysiloxanes with One to Four Silicon Atoms*

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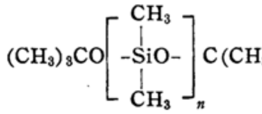
Ethoxy end-blocked dimethylpolysiloxanes[2] have been prepared by the partial hydrolysis of dimethyldiethoxysilane. Also, the lower members of methoxy[3] and isopropoxy[4] end-blocked dimethylpolysiloxanes have been prepared by the sodium bicarbonate treatment of partially methanolyzed and *iso*-propanolyzed dimethyldichlorosilane respectively. In this paper, we wish to report on the preparation and properties of *tert*-butoxy end-blocked dimethylpolysiloxanes as indicated by formula T_n.

T_n:



$$(CH_3)_3CO\left[-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{Si}}}}O-\right]_n C(CH_3)_3 \quad (n=1-4)$$

The higher members of the series T_n may be synthesized by the partial hydrolysis of dimethyldi-*tert*-butoxysilane. In this paper, two other routes of preparation will be reported. It has been known that *tert*-butanol does not react with chlorosilanes without an acid acceptor to form *tert*-butoxysilanes. Accordingly, an equivalent amount of pyridine to chlorosilane was used as an acid acceptor in these experiments. In the first route, dimethyldichlorosilane was added to the mixture of aqueous *tert*-butanol, pyridine and benzene. After refluxing, the pyridine hydrochloride was dissolved with an excessive amount of water and the separated organic layer was fractionated. In this route, the water in the reaction medium reacted with dimethyldichlorosilane more rapidly and there was obtained a relatively large amount of dimethylcyclopolysiloxanes (D_n) in the product. D_n distilled out between the plateaus of linear polymers, T_{n-3} and T_{n-2}, and the lower members of these polymers were not difficult to separate, but the separation was supposed to become difficult with the increasing polymer size. In a hope of obtaining the linear polymers with the formation of as small an amount of cyclopolymers as possible, the following second route was carried out.

In the second route, dimethyldichlorosilane was added to the mixture of pyridine, benzene and various insufficient amounts of *tert*-butanol and refluxed to complete the alcoholysis. By adding excess of water to the product, dissolving of the pyridine hydrochloride and hydrolysis of the remaining Si—Cl were carried out at the same time. Fractionation gave a small amount of crystalline solid with the fraction of T_2. This crystalline solid was confirmed to be tetramethyldisiloxane-1,3-diol. It is interesting to note that an unstable diol is obtained through the distillation. The higher diols were also supposed to be present at the fore part of the plateaus of T_n (n=3,4 and 5), considering from the higher refractive index at this part, but they could not be isolated. The amount of this crystalline diol was decreased by redistillation or by refluxing the partially alcoholyzed product with a slight excess of water to convert the remaining Si—Cl into Si—O. Properties of T_n are shown in Table I.

Experimental

Starting Materials.— Dimethyldichlorosilane supplied by Shin-etsu Chem. Ind. Co. and *tert*-butanol of Shell Chemicals were used without further purification.

Reaction of Dimethyldichlorosilane with Aqueous *tert*-Butanol.—A mixture of pyridine (0.4 mole), benzene (50 g.), *tert*-butanol ($x^*=2$ to 1) and water ($0.2\times(2-x)/2$ mole) was placed in a 300 cc. three-necked flask equipped with an efficient stirrer, a dropping funnel and a reflux condenser. Dimethyldichlorosilane (0.2 mole) was added drop by drop with vigorous

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[1] Part VI of this series, R. Ōkawara, G. Minami and Z. Oku, This Bulletin, **31**, 22 (1958).

[2] H. J. Fletcher and M. J. Hunter, *J. Am. Chem. Soc.*, **71**, 2918 (1949).

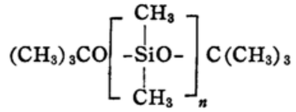
[3] T. Tanaka and R. Ōkawara, This Bulletin, **28**, 364 (1955).

[4] R. Ōkawara, T. Ando and K. Ayama, *Technol. Repts. Osaka Univ.*, **8**, 171 (1958).

* x indicates molar ratios: *tert*-butanol/ dimethyldichlorosilane

TABLE I

tert-BUTOXY END-BLOCKED DIMETHYLPOLYSILOXANES:



$$(CH_3)_3CO\left[\begin{array}{c} CH_3 \\ | \\ -SiO- \\ | \\ CH_3 \end{array}\right]_n C(CH_3)_3$$

Polymer Size $n=$	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.)
1	50.5/15	0.8295	1.3970	59.34 (59.58)	202 (204.39)	13.72 (13.74)
2	85/15	0.8666	1.4001	77.94 (78.22)	276 (278.55)	20.20 (20.17)
3	115/15	0.8936	1.4010	95.90 (96.86)	353 (352.71)	23.98 (23.89)
4	95/1	0.9178	1.4025	113.37 (115.50)	430 (426.87)	26.10 (26.32)

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

** Cryoscopic measurements in benzene.

stirring to the mixture which was cooled with an ice-bath. After the addition the mixture was refluxed for one hour with stirring. An excessive amount of water was added to the mixture which was cooled with a water-bath to dissolve the precipitated pyridine hydrochloride. The separated benzene layer was thoroughly washed with 50 cc. water over five times to separate the dissolved chloride completely. The organic layer was dehydrated with sodium sulfate and simply distilled to drive off benzene, *tert*-butanol and pyridine. The composition of the oily product (Yield: ca. 45—60%) was determined by fractionation through a Stedman column of about 30 theoretical plates. The crystalline hexamethylcyclotrisiloxane (D_3) distilled out at first, the amount of which increased with decreasing x, and then the fraction of monomer (T_1) distilled out, the amount of which decreased from 90 to 55% of the product as x became 2 to 1. All the fractions higher than T_1 and residues thus obtained were united and distilled through the same column. Succeeding to the plateau of T_1, there was found a small plateau of octamethylcyclotetrasiloxane (D_4) at the boiling point of 82°—83°C/35 mm. n_D^{20} 1.3961 (Reported[5]): b. p. 175°C, n_D^{20} 1.3968)

Hydrolysis of Partially *tert*-Butanolyzed Dimethyldichlorosilane.—An insufficient amount of *tert*-butanol ($x=1.6$, 1.2 and 0.8) without water was caused to react with dimethyldichlorosilane (0.2 mole) under the same conditions as described above. By adding water, hydrolysis and dissolving of pyridine hydrochloride were carried out at the same time. Crystals of D_3 were not found in the product of experiments when x is 1.6 or 1.2, but they were found when x is 0.8. When x is 1.2, a portion having a slightly higher refractive index was found at the fore part of the plateau of T_2, and when x is 0.8, a small amount of a crystalline solid was found in that part and the portion which dissolved the crystals showed a higher refractive index than T_2.

To obtain a sufficient amount to characterize this crystalline solid, the alcoholysis was carried out with the same conditions by the use of a larger amount of the starting materials, i. e. 1 mole of dimethyldichlorosilane and 1.2 moles of *tert*-butanol ($x=1.2$). To the mixture, water (9 g.) was added and refluxed for ten minutes with stirring. Fractionation of the product (Yield: 45%) gave a large amount of solid with T_2. The recrystallized solid from benzene-ether mixture having m. p. 63°～65°C and specific gravity 1.118 at 16°C, which was determined by flotation method in the mixture of carbon tetrachloride and benzene, was identified to be tetramethyldisiloxane-1, 3-diol (Reported[6]): m. p. 67°～68°C).

Anal. Found: C, 29.41; H, 8.66%. Calcd. for $C_4H_{14}O_3Si_2$: C, 28.91; H, 8.49%.

Further fractionation gave T_3, but no plateaus higher than this could be obtained. Accordingly, starting with 1 mole of dimethyldichlorosilane and 1 mole of *tert*-butanol, refluxing was carried out after addition of water (11 g.) for thirty minutes to condense diol. Fractionation of the product (Yield: 50%) gave plateaus of T_1 and then D_4. The refractive indices of T_1 and D_4 are nearly the same but the boiling points are so different that T_1 may be separated from D_4 by distillation. Also, a small plateau succeeding to the fraction of T_2 would be assigned to that of D_5. Above T_2, the portion having the higher refractive index was found at the fore part of the plateau, which was supposed to be caused by a contamination of dimethylpolysiloxane-α,ω-diol. As to T_4 (in Table I) and T_5 (b. p. 113°C/1 mm., d_4^{20} 0.9311, n_D^{20} 1.4055. *Anal.* Found: Si, 28.31%. Calcd. for T_5: Si, 28.03%), though small in amount, they were separated but the amount was not enough to be taken as pure compounds,

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

[6] G. R. Lucas and R. W. Martin, ibid., **74**, 5225 (1952).

in view of the question from the increment of refractive index and analysis of silicon.

Analysis of Silicon.—Samples were weighed in gelatin capsule[7] and decomposed by concentrated sulfuric acid.

Summary

1) *tert*-Butoxy end-blocked dimethylpolysiloxanes were prepared from dimethyldichlorosilane, *tert*-butanol and water by the use of pyridine as an acid acceptor.

2) The lower members of those polysiloxanes having one to four silicon atoms were characterized.

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[7] T. Tanaka and R. Ōkawara, This Bulletin, **28**, 364 (1955).