Acknowledgments.—We are indebted to the Minnesota Mining and Manufacturing Co. and The Miner Laboratories for a research grant which made this work possible. We thank R. N. Walter of this Laboratory for the analyses.

Summary

1. Triethylsilanol was prepared in good yield from triethylsilyl sulfate and from triethylchlorosilane.

2. Hydrolysis of trimethylfluorosilane gave trimethylsilanol in excellent yield.

3. Reactions of triethylsilanol and trimethylsilanol have been studied.

4. Formation of the sodium salt from trimethylsilanol and aqueous alkali, and the activity of both silanols with sodium, indicate that the hydrogen of the silicon–hydroxyl group is more reactive than that of the carbon–hydroxyl in tertiary alcohols.

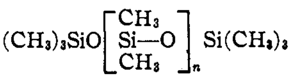
STATE COLLEGE, PA. RECEIVED MARCH 29, 1946

[CONTRIBUTION FROM DOW CORNING CORPORATION]

Organosilicon Polymers. II. The Open Chain Dimethylsiloxanes with Trimethylsiloxy End Groups[1]

BY M. J. HUNTER,[2] E. L. WARRICK,[3] J. F. HYDE[4] AND C. C. CURRIE[2]

In a recent paper[5] the preparation and properties of a series of low polymer cyclic dimethylsiloxanes were described. It was indicated that other series of open chain polymers would be reported at a later date. This paper will describe the series of open chain dimethylsiloxanes with trimethylsiloxy end groups represented by Formula I



$$(CH_3)_3SiO\left[\begin{matrix}CH_3\\ Si{-}O\\ CH_3\end{matrix}\right]_n Si(CH_3)_3 \qquad (I)$$

where n may vary from one to a very large number.

At the time this paper was completed and ready for submission, several articles by Patnode and Wilcock,[6] Hurd,[7] and Wilcock[8] appeared describing polymers of this series and showing some of the interesting physicochemical properties of these materials.

Open chain silicon–oxygen–silicon polymers are well known in mineral silicate chemistry[9] where they form the skeletal structures of such materials as pyroxenes and amphiboles. These silicon–oxygen–silicon open chains are substituted with metal oxide ions on the two remaining positions of each silicon in the chain.

Other inorganic low polymer siloxane chains have been described by Schumb and Holloway,[10] who isolated chains containing six and seven silicon atoms separated by alternate oxygen atoms with chlorine groups satisfying all the remaining silicon valences.

Organo-silicon open chain polymers were first described by Kipping,[11] who isolated a series of polydiphenylsiloxane low polymer units with hydroxyl end groups. Due to the relative instability of the hydroxyl groups, these linear polymers are readily converted into other diphenylsiloxane configurations.

Low Polymer Open Chain Siloxanes

Low polymer disubstituted siloxanes may be divided into three classes: (1) the cyclic members, similar to those previously described,[5,6] (2) open chain polymers with temporary or reactive end groups similar to the hydroxyl terminated polymers described by Kipping,[11] and (3) linear polymers with permanent end groups which show a high relative stability to both heat and moisture. Copolymer chains of dimethylsiloxane units with trimethylsiloxy end groups fall into this third class of polymers.

The methyl polysiloxanes of Formula I may be prepared by cohydrolyzing a mixture of ethoxytrimethylsilane[12] and diethoxydimethylsilane.[13] The condensation products from this reaction, when equal molar mixtures of the two silane intermediates are employed, form a water-white fluid which is approximately 95% distillable. Somewhat similar copolymer mixtures may be obtained from the cohydrolysis of chlorotrimethylsilane[14] and dichlorodimethylsilane[15] which was also pointed out by Patnode and Wilcock.[7] A third method for preparing these compounds is that described by the above authors[7] who isolated them from the rearrangement products of hexamethyldisiloxane and octamethylcyclotetrasiloxane, after treatment with sulfuric acid.

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[1] Presented in large part before the High Polymer Conference at Gibson Island, June 25, 1945, by E. L. Warrick.

[2] Dow Corning Corporation, Midland, Michigan.

[3] Mellon Institute, Pittsburgh, Pennsylvania.

[4] Corning Glass Works, Corning, New York.

[5] Hunter, Hyde, Warrick and Fletcher, THIS JOURNAL, **68**, 667 (1946).

[6] Patnode and Wilcock, THIS JOURNAL, **68**, 358 (1946).

[7] Hurd, *ibid.*, **68**, 364 (1946).

[8] Wilcock, *ibid.*, **68**, 691 (1946).

[9] Bragg, "Atomic Structure of Minerals," Cornell University Press, Ithaca, N. Y., 1937, pp. 139–146.

[10] Schumb and Holloway, THIS JOURNAL, **63**, 2753 (1941).

[11] Kipping, *J. Chem. Soc.*, **101**, 2108–2125 (1912).

[12] Daudt, U. S. Patent 2,390,518, Dec. 11, 1945.

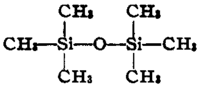
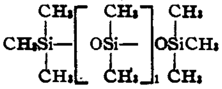
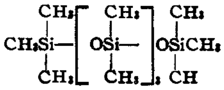
[13] McGregor and Warrick, U. S. Patent 2,380,057, July 10, 1945.

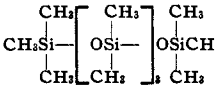
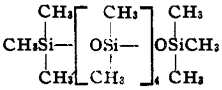
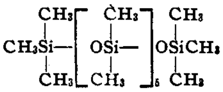
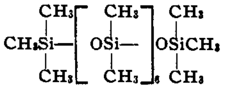
[14] (a) Taylor and Walden, THIS JOURNAL, **66**, 842 (1944); (b) Gilliam and Sauer, *ibid.*, **66**, 1793 (1944); (c) McGregor and Warrick, U. S. Patent 2,386,488, Oct. 9, 1945.

[15] (a) Gilliam, Liebhafsky and Winslow, THIS JOURNAL, **63**, 801 (1941); (b) Rochow, U. S. Patent 2,286,793, June 16, 1942.

TABLE I

PHYSICAL PROPERTIES OF ANALYSIS OF OPEN CHAIN DIMETHYLSILOXANE POLYMERS WITH TRIMETHYLSILOXY END GROUPS

1	Polymer size	Dimer	Trimer	Tetramer
2	Name	Hexamethyldisiloxane	Octamethyltrisiloxane	Decamethyltetrasiloxane
3	Formula	 $CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-CH_3$	 $CH_3\overset{CH_3}{\underset{CH_3}{Si}}-\left[O\overset{CH_3}{\underset{CH_3}{Si}}-\right]_1 O\overset{CH_3}{\underset{CH_3}{Si}}CH_3$	 $CH_3\overset{CH_3}{\underset{CH_3}{Si}}-\left[O\overset{CH_3}{\underset{CH_3}{Si}}-\right]_2 O\overset{CH_3}{\underset{CH}{Si}}CH_3$
4	B. p., °C.	99.5	152	192
5	M. p., °C.	−68	−86	−76
6	Vis. centistokes at 25°	0.65	1.04	1.53
7	Sp. gr. 25°/25°	0.7606	0.8182	0.8516
8	Ref. index, 25°	1.3748	1.3822	1.3872
9	Molar refraction	48.89	67.48	86.15
10	Atomic refr. of Si	6.518	6.25	6.10
11	Molar refr. calcd. from bond refractivities	48.92	67.56	86.20
12	Surf. tens. dynes/cm. 25°	14.82	16.05	16.52
13	Parachor	420.22	580.14	737.4
14	Parachor equiv. for Si	31.81	30.44	29.1
15	Coeff. of exp., $B \times 10^3$ = (25–100°)	1.598	1.451	1.312
16	Victor Meyer mol. wt.	159	222	301
17	Mol. wt. cyclohexane f. p. dep.	174	243	318
18	Mol. wt. calcd.	162.24	236.34	310.44
19	% Carbon found	44.10	39.80	39.30
20	% Carbon calcd.	44.40	40.60	38.70
21	% Silicon found	34.35	35.4	36.07
22	% Silicon calcd.	34.50	35.5	36.10

1	Polymer size	Pentamer	Hexamer	Heptamer	Octamer
2	Name	Dodecamethylpentasiloxane	Tetradecamethylhexasiloxane	Hexadecamethylheptasiloxane	Octadecamethyloctasiloxane
3	Formula	 $CH_3\overset{CH_3}{\underset{CH_3}{Si}}-\left[O\overset{CH_3}{\underset{CH_3}{Si}}-\right]_3 O\overset{CH_3}{\underset{CH_3}{Si}}CH_3$	 $CH_3\overset{CH_3}{\underset{CH_3}{Si}}-\left[O\overset{CH_3}{\underset{CH_3}{Si}}-\right]_4 O\overset{CH_3}{\underset{CH_3}{Si}}CH_3$	 $CH_3\overset{CH_3}{\underset{CH_3}{Si}}-\left[O\overset{CH_3}{\underset{CH_3}{Si}}-\right]_5 O\overset{CH_3}{\underset{CH_3}{Si}}CH_3$	 $CH_3\overset{CH_3}{\underset{CH_3}{Si}}-\left[O\overset{CH_3}{\underset{CH_3}{Si}}-\right]_6 O\overset{CH_3}{\underset{CH_3}{Si}}CH_3$
4	B. p., °C.				
5	M. p., °C.	−84	−59	−78	−63
6	Vis. centistokes at 25°	2.06	2.63	3.24	3.88
7	Sp. gr. 25°/25°	0.8710	0.8873	0.9004	0.9078
8	Ref. index, 25°	1.3902	1.3922	1.3940	1.3952
9	Molar refraction	105.06	123.56	142.98	160.88
10	Atomic refr. of Si	6.05	5.96	5.83	5.79
11	Molar refr. calcd. from bond refractivities	104.84	123.48	142.12	160.76
12	Surf. tens. dynes/cm. 25°	17.08	17.42	17.61	18.03
13	Parachor	900.06	1059.5	1217.3	1381.1
14	Parachor equiv. for Si	29.48	29.02	28.53	28.91
15	Coeff. of exp., $B \times 10^3$ = (25–100°)	1.247	1.206	1.154	1.136
16	Victor Meyer mol. wt.	377	458		
17	Mol. wt. cyclohexane f. p. dep.	391	479	540	620
18	Mol. wt. calcd.	384.54	458.64	532.74	606.84
19	% Carbon found	37.40	36.55	35.93	35.7
20	% Carbon calcd.	37.30	36.65	36.15	35.6
21	% Silicon found	36.40	36.70	36.60	....
22	% Silicon calcd.	36.50	36.7	36.81	37.1

Cohydrolysis of the above mixture of $(CH_3)_2SiO(C_2H_5)_2$ and $(CH_3)_3SiOC_2H_5$ produces a series of polymers which are indicated by the progressively higher boiling plateaus shown in Fig. 1. The first plateau represents hexamethyldisiloxane.[16] The subsequent compounds are open chain dimethylsiloxane polymers with trimethylsiloxy end groups. Analyses and physical properties of the redistilled compounds, from the plateaus indicated in Fig. 1, are shown in Table I.

Since in no instance do the boiling points of the cyclic dimethylsiloxanes coincide with those of the lower members of the open chain polymer series, it is possible to obtain good separation of the two types of structures by fractional distillation. The small inflection shown in Fig. 1 between the open chain trimer and tetramer is the cyclic tetramer. The amount of cyclic tetramer obtained is related to the probability of four dimethylsiloxane units forming a chain and cyclicizing before either end reacts with a chain terminating trimethylsiloxy group. Since this is the most probable cyclic,[5] the plateaus shown are believed to be relatively free from cyclic contamination.

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[16] (a) Sauer, THIS JOURNAL, 66, 1707 (1944); (b) Daudt, U. S. Patent 2,386,441, Oct. 9, 1945.

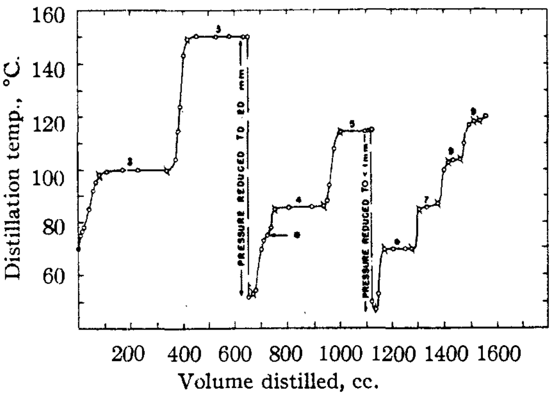

Fig. 1.—Fractional distillation curve from mixed open-chain low polymers obtained by cohydrolyzing equal moles of diethoxydimethylsilane and ethoxytrimethylsilane. Numbers on plateaus refer to the number of silicon atoms in each open chain compound. * Arrow points to yield of cyclic tetramer.

The complete vapor pressure curves for this series of highly purified open chain polymers are found on the Cox chart (Fig. 2), and are quite similar to the series of curves given in the previous paper for the cyclic dimethylsiloxanes. The marked similarity of vapor pressure characteristics of the cyclic and linear forms may be shown in another way by plotting the atmospheric boiling points of these two series of compounds against their molecular weights as shown in Fig. 3. It is evident that the difference in molecular weight and not the difference in geometric structure between cyclic and open chain polymers is the important factor in determining boiling points.

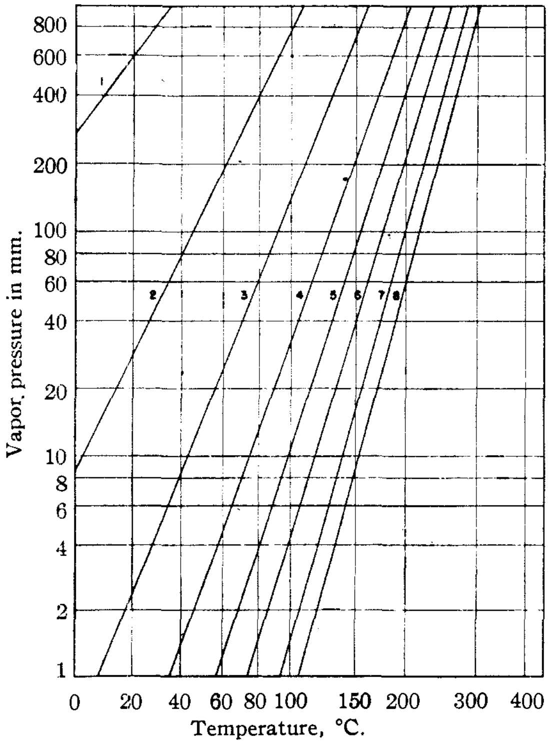

Fig. 2.—Cox chart curves for trimethylsiloxy end blocked dimethylsiloxane low polymers. Numbers refer to number of silicon atoms in each compound. Curve 1 is tetramethylsilane.

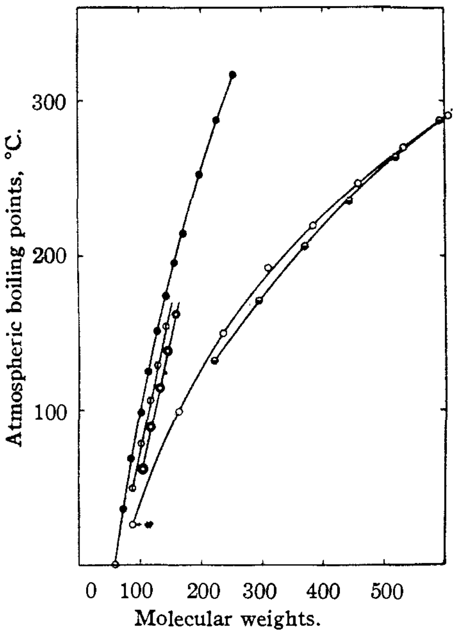

Fig. 3.—Comparison of the boiling points of dimethylsiloxanes with normal hydrocarbons having comparable molecular weights: ●, normal hydrocarbons; ○, open chain polymers; ⊖, cyclic polymers; ⦶, branched alkanes[18]; ⊙, tetraalkylsilanes[18]; *, tetramethylsilane.

Comparison of the boiling points of normal alkanes, branched alkanes and the corresponding tetralkylsilanes, presented by Whitmore, *et al.*,[17] with the methylsiloxanes is shown in Fig. 3. It is apparent that the dependence of boiling point on molecular weight is about the same in both the normal alkane and the branched alkane series. Likewise, the introduction of a silicon atom into a branched alkane alters the boiling point dependence only slightly. The siloxane systems which contain silicon–oxygen structures, however, have phenomenally different dependence of boiling point on molecular weight. It is clear that the presence of the siloxane structure is responsible for these marked differences.

The freezing points of the two series of polymers are plotted in Fig. 4. Both series show the alternating effect of odd and even numbered structures on the freezing point as a demonstration of symmetry. The cyclic trimer of dimethylsiloxane is an exception and may be explained by the planar nature of this ring.[18] The open chain linear polymers have a greater number of possible configurations and so a decreased probability of being in an oriented form results in the much

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[17] Whitmore, Sommer, DiGiorgio, Strong, Van Strien, Bailey, Hall, Pietrusza and Kerr, THIS JOURNAL, **68**, 475 (1946).

[18] Frevel and Hunter, *ibid.*, **67**, 2275 (1945).

lower freezing points compared with the corresponding cyclic systems.

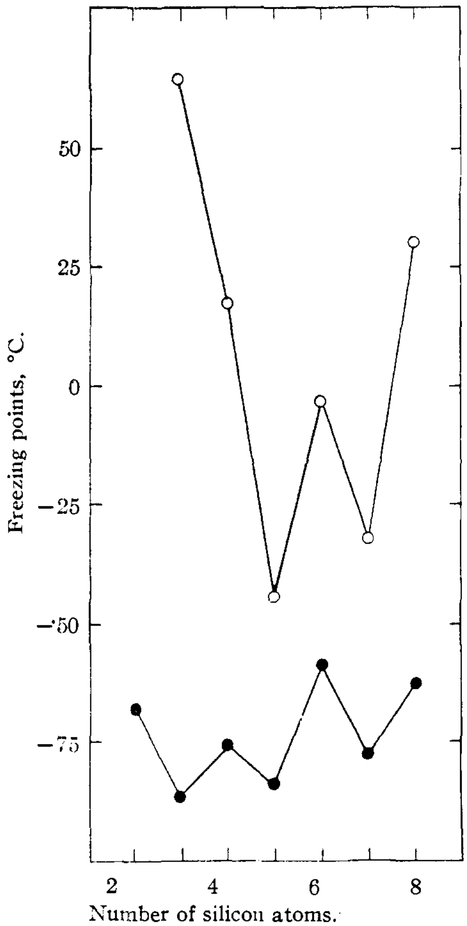

Fig. 4.—Comparison of the freezing points of open chain with cyclic polymers; ●, open chain structures; O, cyclic structures.

Viscosities of these two series of siloxane polymers may be compared by noting the curves of Fig. 5. This is an outstanding example of the effect of the shape of a molecule on the viscosity in the liquid state. From certain fundamental considerations, Hurd[6] has recognized the same phenomenon. The low molecular weight members of both the cyclic and linear series have about the same viscosities (*e.g.*, four-membered polymers), but as the size increases the space required for the motion of the cyclics becomes much greater and their viscosities increase much more rapidly. A further comparison of the viscosities of these siloxane polymers with those of the saturated hydrocarbons may be noted in the same figure. The data for hydrocarbons are taken from the paper by Kierstead and Turkevich.[19] Dimethylsiloxanes in general have much lower viscosities at 25° than the saturated hydrocarbons of corresponding molecular weight. The effect of structure, cyclics compared with linear, is evident in the hydrocarbons as in the siloxanes.

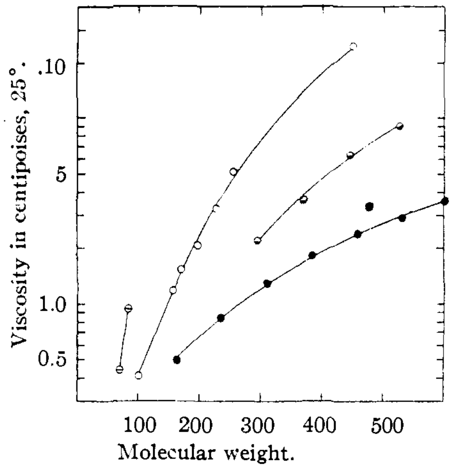

Fig. 5.—Variation of viscosity with molecular weights of dimethylsiloxane polymers and hydrocarbons showing the effect of cyclic and open chain structures: ●, dimethylsiloxane open chains; ◒, dimethylsiloxane cyclics; O, normal alkanes; ⊖, cyclic alkanes.

Density variations of the open chain siloxane polymers found in Table I are greater from one member to the next than was found in the members of the cyclic dimethylsiloxane series previously reported. This is a result of decreasing the carbon content of the molecule or, in other words, it shows the effect of diluting the end group with dimethylsiloxane units. Such an effect was not present in the cyclic series where the chemical composition remained constant.

The molar refractions listed in line 9 of Table I may be used to obtain the atomic refractions of silicon as listed in line 10. It will be seen that this is not a constant for silicon, but is dependent upon the average degree of substitution of organic groups on the silicon. An inspection of the literature shows that not only is the atomic refraction of silicon dependent on the degree of substitution, but that it is also quite dependent on the kind of substituent. This may result because the bonds formed between silicon and most other atoms are more highly ionic than those of carbon with corresponding atoms.[20] It should be noted from this series that the average atomic refraction for silicon is gradually lowered from one member to the next as the per cent. of carbon–silicon bonds (11.5% ionic in character) is decreased and the per cent. of silicon–oxygen bonds (50% ionic in character) is increased. Denbigh[21] has shown that the molar refraction of a molecule may be considered to be an additive property of the bonds rather than of atoms of which it is composed. Following his method, the refraction of a silicon–carbon bond where the carbon is aliphatic has

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(19) Kierstead and Turkevich, *J. Chem. Phys.*, **12**, 24 (1944).

(20) Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, pp. 39–40, 59–70, 210.

(21) Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

been found to be 2.50 ml./mole and similarly silicon–oxygen has a value of 1.75 ml./mole. Using these values and that of Denbigh for carbon–hydrogen (1.69 ml./mole) the molar refractions of the open chain polymers have been calculated and are listed in line 11 of Table I. The per cent. error in calculating such values as compared with those observed is less than 0.5% in all of the above examples. Similar calculations for the cyclics yield molar refractions with less than 0.25% error compared to the observed values.

The application of bond refraction data to organosilicon chemistry eliminates the necessity for using a variable atomic refraction for silicon and makes possible the calculation of molar refractions for unknown compounds, especially those containing silicon atoms with different types of substituents. The bond refractivities for other silicon bonds have been calculated and will be compared to literature values of molar refraction in subsequent publications.

The surface tensions of the open chain linear siloxane polymers were determined and were found to be lower than those reported for the corresponding cyclic dimethylsiloxanes. From these data, the parachors and parachor equivalents for silicon in open chain dimethylsiloxane polymers have been calculated using the values obtained from Glasstone.[22] The results are found in Table I, lines 13 and 14. The changing parachor equivalent for silicon might be reconciled if bond parachors were available for use in a manner similar to that outlined by Denbigh for bond refractions. In the absence of bond parachors, it is evident that the silicon atoms with the greatest number of silicon–oxygen bonds have the smallest parachor equivalents.

High Polymer Dimethylsiloxanes

The low polymer linear dimethylsiloxanes described above comprise the lower range of a polymer homologous series in which *n* may vary from one to a very large number. Fluids with progressively higher molecular weights in this series may be prepared in a controlled manner to cover all viscosity ranges from those just described up to completely non-volatile highly viscous materials. This is accomplished by calculating the mole per cent. of end-group necessary to yield the average chain length desired. Molecular weights of a series of fluids plotted against viscosity are shown in Fig. 6 using data obtained by Barry.[23] The properties of this series of stable open chain dimethylsiloxane polymers with increasing average molecular weights are shown in Table II.

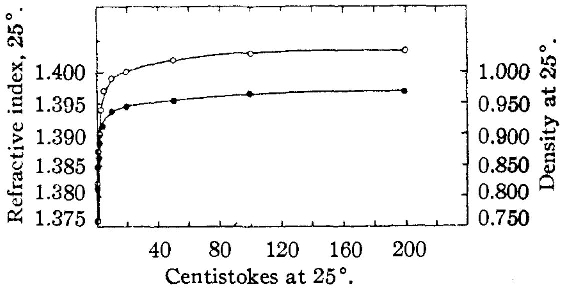

Fig. 6.—Comparison of refractive index and densities of open chain polymers showing the effect of diluting the end group: ●, densities of open chain polymers; O, refractive index of open chain polymers.

Table II

Physical Properties of Linear High Polymers

Visc. Centistokes, 25°C.	A. S. T. M. pour point	Density 25°C.	Refr. index, 25°C.	Approx.[a] mol. wt.	Exp. coeff. $K \times 1000$ per °C. 25 to 100°C.
10	−67	0.937	1.399	1200	1.035
20	−60	.947	1.400	1900	1.025
50	−55	.952	1.402	3700	1.000
100	−55	.965	1.4030	6700	0.969
200	−53	.968	1.4031	11300	.968
350	−50	.969	1.4032	15800	.966
500	−50	.969	1.4033	19000	.965
1000	−50	.970	1.4035	26400	.963

[a] Calculated from intrinsic viscosity data by Barry.[23]

In the lower polymer ranges, one can readily observe the effect of the trimethylsiloxy end group on the physical properties, refractive index and density, as shown in Fig. 5, but in polymers above twenty to twenty-five units, these properties vary only slightly with increasing molecular weights. Viscosity relationships, on the other hand, show an effect of nearly the opposite nature where small increases in molecular weight cause progressively greater increases as shown in Fig. 7.

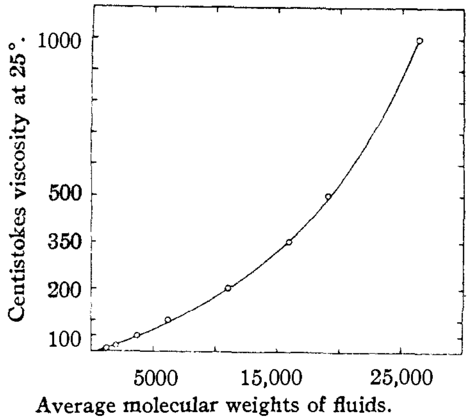

Fig. 7.—Relation between fluid viscosities and average molecular weights of trimethylsiloxy end blocked dimethylsiloxanes.

Freezing points for these high polymers are not sharp because of the distribution of molecular weights in a given viscosity fluid. For this reason, A. S. T. M. pour points are quoted instead. These

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[22] Glasstone, "Textbook of Physical Chemistry," D. Van Nostrand Co., New York, N. Y., 1940, p. 516.

[23] Barry, "Viscometric Investigation of Dimethylsiloxane Polymers," presented before the High Polymer Division of the American Physical Society, New York, N. Y., January 26, 1946.

values show the tendency of the freezing point to rise as polymer size increases and to approach the value for high polymers asymptotically.

Experimental

Preparation of Low Polymer Mixtures.—In a five-liter three-necked flask fitted with a reflux condenser and agitator was placed 1393 g. (9.41) moles of diethoxydimethylsilane[13] and 1110 g. (9.41 moles) of ethoxytrimethylsilane.[12] To this solution was added 254 g. (14.11 moles) of water containing 7.5 g. of sodium hydroxide. The mixture was heated to 40° and the temperature continued to rise spontaneously to 60–65° in about an hour. After adding 50 cc. more water (20% excess) the mixture was refluxed for two hours.

Alcohol was distilled from the mixture until the temperature of the oily residue reached 100°. The distillate weighed 1706 g. (theory = 1430 g.). When this distillate was poured into four times its volume of water, an insoluble oil separated (457 g.). This was added back to the original oil and the combined fluid refluxed for two hours with 550 cc. of 20% hydrochloric acid for the purpose of removing the last traces of ethoxyl groups. The oil layer was then washed with distilled water until neutral; yield 1426 g. (calcd. 1469 g.).

The mixed polymer fluid was distilled through a fractionating column, 4 ft. × 1.25 in. packed with 0.25 in. glass helices, at ten to one reflux ratio with a Corad[24] head. This gave a distillation curve. Data shown in Table I were taken from carefully redistilled members of this series of compounds. A residue of 178 g. (12.4%) was strip distilled giving a final non-volatile residue of 39.1 g. (2.75%). The viscosity of the volatile portion was 6.64 centistokes and the final residue 12.0 centistokes.

Copolymerization with 2.5 Mole End-Group.—In a one-liter, three-necked flask equipped with a stirrer, dropping funnel, thermometer and reflux condenser was placed 288.6 g. (1.95 moles) of diethoxydimethylsilane and 5.9 g. (0.05 mole) of ethoxytrimethylsilane. To this was added through the dropping funnel 36 g. of water containing 0.2 g. of sodium hydroxide over a period of thirty minutes with good agitation. The temperature rose spontaneously from 25 to 60° in about one hour. The reflux condenser was then exchanged for a downward condenser and alcohol distilled off by the application of heat until the temperature of the residue rose to 100° (alcohol yield, 169 g.; calcd., 180 g.). To the oily residue was added 150 cc. of 20% hydrochloric acid and the mixture was refluxed for four hours. The oil and acid layers were separated and the siloxane fluid was washed with water until free from acid. When the fluid was heated to 250° at 1 mm. pressure under distillation conditions, there remained a water-white fluid residue of 123.4 g. (83%) with a viscosity of 81 centistokes at 25°.

Copolymerization with 5.0 Mole Per Cent. End-Group.—In a similar run made with 5.0 mole% of ethoxytrimethylsilane there was obtained an 87.3% yield of non-volatile fluid with a viscosity of 38.6 centistokes at 25°.

Theoretical Discussion

The low boiling points of these compounds as contrasted with saturated hydrocarbons of similar molecular weight seem to be evidence of low molecular cohesive forces. The slopes of the vapor pressure curves in Fig. 2 are not truly heats of vaporization but are closely related to them. From these slopes a reasonably constant difference of 960 cal. is found in going from one member to the next. This is presumably the contribution of a $(CH_3)_2SiO$ group to the over-all molecular cohesion and agrees quite well with the cyclic dimethylsiloxanes. It was pointed out in the previous paper[5] that Dunkel[25] has shown these slopes to be additive in terms of the contribution of atoms or groups to the over-all molecular cohesion of organic compounds. The vapor pressures of many organic compounds could be predicted by his methods. An attempt to calculate the contribution of the $(CH_3)_2SiO$ unit from Dunkel's data, however, gave a value of 5190 cal. exclusive of silicon.

The contribution of a trimethylsiloxy group may be estimated as half of the slope value for the first member of the open chain series, hexamethyldisiloxane, or 4560 cal. Calculated from Dunkel's data, the trimethylsiloxy group should contribute roughly 6150 cal. exclusive of silicon.

The slope of the vapor pressure curve for tetramethylsilane is about 5900 cal. and the calculated value from Dunkel's data is 7120 cal. exclusive of silicon. The influence of silicon–oxygen bonds on the contribution of these groups is summarized in Table III.

TABLE III

MOLAR COHESION

Group	Slope of the vapor pressure curve, cal. Obs.	Calcd.[a]	Ratio obs./calcd.
$Si(CH_3)_4$	5920	7120	0.835
$Si(CH_3)_3O_{1/2}$	4560	6150	.74
$Si(CH_3)_2O$	960	5190	.185

[a] From Dunkel's data exclusive of silicon.

It is apparent that the presence of silicon–oxygen bonds greatly decreases the contribution of the various groups from the values expected on the basis of hydrocarbon data. This is a further illustration of the phenomenon pointed out in Fig. 3 where the increase in oxygen content of a polymer progressively increased the deviation of siloxane boiling points from those of the saturated hydrocarbons and tetraalkylsilanes of corresponding molecular weights.

The influence of the silicon–oxygen bond may be illustrated by the slight effect of temperature on the viscosity of these polymers. Based on the Eyring treatment of viscous flow, Kierstead and Turkevich[19] have derived an Arrhenius type equation which they have applied to fluidity.

$$\text{Fluidity} = Ae^{-E/RT}$$

The calculations for the cyclic dimethylsiloxanes were previously reported[5] and similar data for the open chain siloxanes are assembled here in Table IV. Similar values were found by Wilcock[8] for the temperature range 100 to 210°F. and by Hurd[7] for the range 25 to 75°. Their data were in centipoises and yield energy of activation terms free of density changes.

The low viscosity temperature slope of these cyclic and open chain polymers may be compared to the behavior of the saturated hydrocarbons in Fig. 8. As the linear siloxane polymers increase

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(24) Catalog L. P. 24, "Pyrex Laboratory Glassware," Corning Glass Works, Corning, New York, 1944, p. 42.

(25) Dunkel, *Z. physik Chem.*, **A138**. 42 (1928).

TABLE IV

ENERGY OF ACTIVATION FOR VISCOUS FLOW OF OPEN CHAIN METHYL SILOXANES OF FORMULA I

Number of Si atoms	$E_{(\text{visc.})}$, cal. Found[a]	Calcd.	Mol. wt.
2	2115	2110	162.32
3	2230	2260	236.45
4	2510	2410	310.58
5	2708	2560	384.71
6	2765	2710	458.84
7	2865	2860	532.96
8	3070	3010	607.09
Normal hydrocarbons			
Pentane	1504		72
Hexane	1690		86
Heptane	1858		100

[a] Over the temperature range −40 to 25° with viscosities in centistokes for the siloxanes.

in size, the energy of activation for viscous flow becomes constant for the non-volatile high polymer dimethylsiloxanes and indicates a flow unit for such polymers of roughly eight siloxane units.

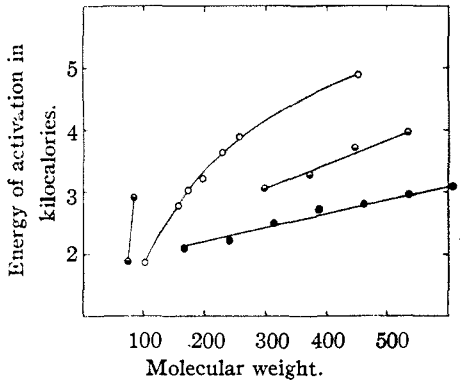

Fig. 8.—Comparison of energy of activation for dimethylsiloxanes with hydrocarbons: ●, open chain siloxanes; ⊖, cyclic siloxanes; ○, normal alkanes; ◒, cyclic alkanes.

The nature of the two dimethylsiloxane series may be indicated further by the value of the ratio E (vap.)/E (flow) which Eyring indicated should be 3.0 for a spherical type molecule and 4.0 for an unsymmetrical chain type molecule.[26] The heats of vaporization may be estimated from the vapor pressure curves by a method of Miles.[27] The average value of the above ratio for the previously reported cyclic dimethylsiloxane series is 3.14 and for the open chain series here reported the value is on the average 4.46.

The average difference in E (flow) values between members of the linear series is about 150 cal. This is considered to be the contribution of a dimethylsiloxane group $(CH_3)_2SiO$ to the over-all energy of activation for viscous flow, and is less than the difference between E values for members of the saturated linear hydrocarbons reported by Kierstead and Turkevich.[19] From their data it is evident that the effect of the methylene groups is additive with respect to their contribution to the value of E (flow) which is approximately 200 cal. and the contribution of a terminal methyl group is about 450 cal. By this method of treatment, the trimethylsiloxy end group contributes about 1055 cal. to the energy of activation for viscous flow. The calculated values in Table IV column (3) were obtained using this value and 150 cal. for the dimethylsiloxane groups.

It is evident that the unit containing the greater number of silicon–oxygen bonds has the smaller contribution to the energy of activation required for viscous flow. This seems to confirm the view that the presence of siloxane bonds is responsible for the low molecular cohesions in the two series of siloxane polymers. The silicon oxygen bonds of about 50% ionic character may be thought of as powerful internal dipoles which act to decrease the external fields of substituent groups, and the general result is a decreased influence of perturbing agents such as light or a reduced effect of force fields of other molecules tending to react with the hydrocarbon portion of the siloxane. Thus the ionic character of the silicon–oxygen bond, in organosilicon systems with increasing silicon–oxygen bond contents, is reflected in the progressive decrease in atomic refraction for silicon, decrease in parachor equivalent for silicon, and the decrease in contribution of organic substituent groups to over-all molar cohesion as measured from vapor pressures and viscosity temperature slopes.

Summary

1. Open chain dimethylsiloxane polymers containing from three to eight silicon atoms with trimethylsiloxy end groups have been prepared and their physical properties reported.

2. The comparative properties of open chain and cyclic dimethylsiloxane structures are discussed.

3. The open chain low polymers are shown to be the first members of an homologous series of polydimethylsiloxanes. The properties of higher members of this series are also described.

4. Many of the phenomenally different properties of dimethylsiloxanes, compared with hydrocarbons and tetralkyl silanes, seem to depend in large part on the ionic character of the silicon–oxygen bond.

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(26) Ewell and Eyring, *J. Chem. Phys.*, **5**, 726 (1937).

(27) Miles, *Ind. Eng. Chem.*, **35**, 1058 (1943).