Organopolysiloxanes Containing Group IV Organometallic Substituents in the Side Chains

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INTRODUCTION

Physical studies of the dimethylpolysiloxanes carried out in recent years have indicated that there is a very low degree of intermolecular attraction between the polysiloxane chains. For a complete discussion of this point the reader is referred to reference (1), Chapters 6 and 7. For our present purposes it may suffice to say that the very low molecular cohesion of liquid polysiloxanes is demonstrated by their comparatively low boiling points, their high molar volumes, their low energies of activation of viscous flow, their low surface tensions, and their high compressibilities. In addition, the softness and flexibility of high molecular weight silicone rubber, the moderate tensile strength of all solid siloxane polymers, and the small changes in elastic modulus of silicone rubber with temperature give further indication of low molecular attraction in solid polysiloxanes.

Previous viscometric studies of polysiloxanes containing polar groups in the side chains seem to indicate that introduction of these groups enhances interchain attraction. (For the purposes of this discussion we shall define a "polar" group as one which is either markedly more positive or markedly more negative with respect to carbon than are the hydrogen atoms of a methyl group.) Thus an increase in the energy of activation of viscous flow was observed in methylpolysiloxanes when some of the methyl groups were replaced by chloromethyl,^{2,3} thiocyanomethyl,⁴ mercaptomethyl,⁵ p-chlorophenyl,⁶ acetoxymethyl,⁷ or hydroxymethyl⁷ groups. Linear methylpolysiloxanes, the terminal silicon atoms of which bore a β -carboethoxyethyl group, also showed a large increase in the energy of activation of viscous flow over the corresponding all-methyl substituted siloxanes.⁸ Not enough examples have been described to permit wide generalizations as to the mechanism by which such polar substituents cause an enhancement of the energy of activation of viscous flow and hence of the intermolecular attraction. However, Roedel³ has ascribed these greater interchain forces to interchain dipole-dipole interactions of the C-Cl dipoles in the case of the chloromethyl-substituted siloxanes. Cooper⁴ has advanced a similar explanation for the enhanced intermolecular attraction found in polysiloxanes with thiccyanomethyl substituents.

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The siloxanes examined previous to the present study all contained polar substituents that are electronegative relative to the hydrogen of a normal alkyl group. It is well known that such electronegative groups tend to make the carbon-silicon bond more unstable toward ionic fission (cf. Rochow,¹ pp. 19–28). This may be explained by the inductive effects operative within the molecule. The relative electronegativities of carbon and silicon are such that in a carbon-silicon bond the electron cloud should be denser nearer the carbon atom:

$$Si \rightarrow C$$

Attachment of an electronegative substituent, X, to the carbon atom should cause the C—Si bond to become more polar in nature, hence more easily cleaved, since the electron-attracting effect of the carbon atom relative to the silicon atom will be reinforced:

$$Si \rightarrow C \rightarrow X$$

On the other hand one would predict that introduction of an electropositive group, Y, would lead to the opposite effect, *i.e.*, it would make the carbonsilicon bond less polar, and therefore, less subject to cleavage, by its inductive effect which opposes that operative in an isolated carbon-silicon bond:

 $Si \rightarrow C \leftarrow Y$

Consideration of the Pauling electronegativity scale⁹ suggests that organometallic substituents of the nontransition metals more electropositive than carbon (B, Be, Al, Si, Ge, Sn, Pb, As, Sb, Te, Ga, In, Bi) would be theoretically suitable as electropositive polar groups in siloxane side chains. The only siloxanes containing substituents electropositive with respect to the normal alkyl group which have previously been employed have been cyclic siloxanes containing the trimethylsilylmethyl group.¹⁰ However, these were not investigated from the standpoint of interest in this study. We have therefore prepared silanes of the type Me₃MCH₂(Me)SiX₂,¹¹ where M is Si, Ge, Sn, or C, and X is a hydrolyzable group such as Cl, OMe, or OEt. We have studied their relative ease of hydrolysis and condensation, and also have studied the viscosity-temperature behavior of linear siloxanes obtained from the hydrolysis products by conventional equilibration procedures.

HYDROLYSES

The polymerizable silanes listed in reference (11) were available for this study. As outlined in the experimental part of this paper, two different methods were used to hydrolyze the silanes, according to the hydrolyzable groups present. The products obtained are described in Table I. The results present an interesting example of the effect of steric hindrance on the condensation of silanols. No difficulties are encountered in the preparation of dimethylpolysiloxanes; indeed, special techniques are required to isolate the intermediate dimethylsilanediol and tetramethyl-1,3-disiloxanediol.^{12,13} On the other hand, complete condensation of silanols containing bulky substituents has been shown to be quite difficult. Thus, iu the most extreme case, it was demonstrated that di-*tert*-butylsilanediol cannot be condensed, even when very drastic conditions are used¹⁴. Condensation of bis(trimethylsilylmethyl)silanediol was somewhat less difficult, requiring treatment with iodine and β -naphthalenesulfonic acid at the boiling point of the xylene solvent for 16 hours to effect 95% condensation.¹⁵

The results of the hydrolysis experiments of the present study indicate that the ease of hydrolysis and condensation in the $Me_3MCH_2(Me)Si(OMe)_2$ series increases as the central atom of the neopentyl-type group increases in size, *i.e.*:

$$C < Si < Ge \sim Sn$$

Identical hydrolysis procedures gave the silanediol from the neopentyl silane, the siloxanediol from the trimethylsilylmethyl silane, and more highly condensed substances from the trimethylgermylmethyl and trimethylstannylmethyl silanes. Consideration of Fischer-Hirshfelder models of the first two members of the series shows that "crowding" due to the steric requirements of the three methyl groups is much greater for the neopentyl group than for the trimethylsilylmethyl group, and it is very probable that the steric hindrance decreases as the size of the central atom of the neopentyl-type group increases. Recent studies¹⁶ by Grubb indicate that silanol condensation is a bimolecular reaction of the $S_N 2$ type. The rates of such reactions are strongly diminished by the presence on the inverting atom of bulky groups which hinder back-side attack by the attacking reagent. The results of this study are in harmony with the proposed mechanism.

EQUILIBRATIONS

For viscometric studies to be discussed in the next section low molecular linear siloxanes of the type:

$Me_3SiO+Si(Me)(R)O+_nSiMe_3$

where R represents the Me₃MCH₂ group and n is 1,2,3, ... were required. In all cases except one, equilibrations of the hydrolysis products mentioned above with hexamethyldisiloxane were carried out in isopropyl alcoholwater solution with a potassium hydroxide catalyst.¹⁷ The ratio of chain terminating, monofunctional hexamethyldisiloxane to the chain extending, bifunctional hydrolysis product bearing the organometallic substituent was so chosen that a relatively large proportion of trisiloxane (n = 1) and smaller amounts of higher siloxanes (n>1) would be obtained. The equilibration products obtained are listed in Table II, together with their physical properties.

No.	Silane	Wt., g.	Method	Composition of product	Wt., g.
1	$Me_{3}SiC_{2}H_{4}(Me)SiCl_{2} \\$	50.0	A	$[Me_3SiC_2H_4(Me)SiO]_3$	9.0
				$[Me_3SiC_2H_4(Me)SiO]_n$	15.2
2	$Me_3SiC_2H_4(Me)Si(OMe)_2$	27.7	A	$[Me_3SiC_2H_4(Me)SiO]_n$	18.0
3	$MeSiCH_2(Me)Si(OMe)_2$	80.0	A	84% recovery of starting terial	, ma-
		70.0	В	$[Me_{3}SiCH_{2}(Me)(OH)Si]_{2}O$	25.9
				[Me ₃ SiCH ₂ (Me)SiO] _n [Me ₂ SiCH ₂ (Me)SO L	10.0 4.5
4	Me ₃ SiCH ₂ (Me) ₂ SiOMe	29.0	H_2SO_4	[Me ₃ SiCH ₂ (Me) ₂ Si] ₂ O	13.5
			method		
5	$Me_3GeCH_2(Me)Si(OMe)_2$	53.6	В	Mixture of $[Me_3GeCH_2(Me)SiO]_n$ and uncondensed ma- terial	
6	$Me_{3}SnCH_{2}(Me)Si(OMe)_{2}$	70.0	В	Mixture of $[Me_3SnCH_2(Me)SiO]_n$ and uncondensed ma- terial	
7	$Me_{3}CCH_{2}(Me)Si(OMe)_{2}$	89.4	В	$Me_{3}CCH_{2}(Me)Si(OH)_{2} \\$	55.3

TABLE I. HYDROLYSIS OF SILANES CONTAINING

 a Si, 11.93%; Sn, 49.98%. b Calcd.: 2.00 g. atom active H per mole. Found: 2.30 g. atom active H per mole.

It is important to point out that these base-catalyzed equilibrations confirm the prediction made above regarding the enhanced stability of the carbon-silicon bond toward reagents such as the hydroxide ion when the α -carbon atom bears an electropositive substituent. No cleavage products were detected in any of the equilibrations carried out, and the desired products were obtained in moderate yield, whereas bases easily cleave chloromethyl groups²⁶ and (under more vigorous conditions) will even cleave methyl groups.27

It was felt desirable to "dilute" the equilibrated products so obtained with additional dimethylsiloxy units in order to examine siloxanes which contained a smaller percentage of (Me(R)SiO) units. For this reason basecatalyzed equilibrations of Me₃SiOSi(Me)(R)OSiMe₃ compounds with octamethylcyclotetrasiloxane were carried out and the higher molecular weight oils so obtained were studied (cf. Table III).

VISCOSITY STUDIES AND DISCUSSION OF RESULTS

Since the energy of activation of viscous flow is a measure of the intermolecular attraction within a liquid, a study of the viscosity-temperature behavior of the siloxanes prepared was undertaken. Since:

$$\log \eta = (E_{\text{visc.}}/2.303RT) + \text{constant}$$

B.p., °C./mm.	$n_{ m D}^{25}$	d_4^{25}	Mol Calc.	l. wt. Found	Carbo Calc.	on, % Found	Hydro Calc.	gen, % Found	OH Cale.	Found
$138-142/\ 0.175$	1.4405	0.903	480	487	44.95	44.98	10.06	10.02		
148-190/0.3	1.4411	0.906		551						
100-200/ 0.1-0.3	1.4375	0.900		572						
127-132/0.1	Crystall stand	ized on ing		<u></u>	38.77	38.65	9.75	9.53		
140-170/0.1	1.4432	0.929		546						
170°/0.1	1.4422 (28°)		585	375						
84-8°/0.7- 0.95	1.4280	0.831			47.00	46.50	11.18	11.22		
90/0.45 95/0.2	1.4640	1.194		—	_	29.84		7.11		5.78
Not distilled	1.4993	1.448				25.45	_	5.93	—	3.57 ^a
M.p. 98.0- 98.8°			_		48.61	48.57	10.88	10.85 ^b		

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the slope of the plot of log η versus 1/T will be $E_{\text{vise}}/2.303R$, hence:

$E_{\rm visc.} = 2.303 \times R \times {\rm slope}$

where R is the gas constant. We have determined the viscosities of our siloxanes at three temperatures and have calculated the energies of activation of viscous flow by this graphic method. The results are summarized in Table IV and are compared with previously determined data on straight methylpolysiloxanes and on siloxanes containing chloromethyl groups. Since we have measured the kinematic viscosity in centistokes and:

kinematic viscosity = absolute viscosity/density

at the temperature of the measurement, it is apparent that our $E_{\text{visc.}}$ values are not independent of density variations.

Of importance in the discussion of this work are the $E_{\rm visc.}$ values and the actual viscosities of the siloxanes studied. A firm basis for comparison is provided by the MDM compounds. The higher polymer fractions are mixtures of siloxanes of varying molecular weight, and the identity of the constituents and their relative proportions present are not known. (Henceforth the abbreviation "M" will be used to denote the monofunctional Me₃SiO_{1/2} unit and "D" will represent the difunctional Me(R)SiO unit, where "R" represents the group containing the organometallic substituent which is under discussion.) Unfortunately, the $E_{\rm visc.}$ value and the

TABLE II

LINEAR POLYSILOXANES CONTAINING GROUP IV ORGANOMETALLIC SUB-STITUENTS IN THE SIDE CHAINS

 $(CH_3)_3SiO[Si(CH_3)(R)O]_nSi(CH_3)_3$

	Boiling range	e	25	125	Mo	d. wt.	
R n	°C.	Mm.	ⁿ D	u4	Found	Calc.	Note
(CH ₃) ₃ SiCH ₂ 2.16	5 90-105	0.1	1.4200	0.872(a) 486		(b)
$(CH_3)_3SiCH_2$ 3.5	>105	0.1	1.4357	0.911	674		(b)
$(CH_3)_3SiCH_2$ 1.0	77-8	1.5-1.6	1.4068	0.838	313	308.6	(c)
(CH ₃) ₃ SiCH ₂ 2.0	95102	0.2	1.4220	0.866	455	454.9	(c)
$(CH_3)_3SiCH_2$ 2.7	120 - 46	0.2	1.4391	0.918	558	_	(c)
$(CH_3)_3GeCH_2$ 1.0	56-8	0.3	1.4200	0.972	359	353	(c)
$(CH_3)_3GeCH_2$ 1.65	2 74-110	0.2	1.4330	1.036	472		(c)
$(CH_3)_3SnCH_2$ 1.0	60	0.1	1.4350	1.078	404	399.3	(c)
$(CH_3)_3SnCH_2$ 1.9	108 - 24	0.1	1.4550	1.195	611		(c)
$(CH_3)_3CCH_2$ 1.0	60 - 4	0.7-0.9	1.4040	0.835	298	292.6	(c)
(CH ₃) ₃ CCH ₂ 2.0'	7 108-40	0.4	1.4176	0.868	432		(c)
$(CH_3)_3SiCH_2CH_2 = 1.0$	70-3	0.5-0.7	1.4121	0.844	328	322.6	(c)
(CH ₃) ₃ SiCH ₂ CH ₂ 1.53	3 70-121	0.1	1.4212	0.872	414		(c)
$(CH_3)_3SiCH_2CH_2 = 2.73$	5 121-95	0.1-0.3	1.4320	0.895	603		(c)

(a) d_4^{28} . (b) Acid-catalyzed equilibration. (c) Base-catalyzed equilibration.

Analyses of Linear Polysiloxanes Containing Group IV Organometallic Substituents in the Side Chains

 $(CH_3)_3SiO[Si(CH_3)(R)O]_nSi(CH_3)_3$

	Carbo	m, %	Hydro	gen, _%
n	Calc.	Found	Calc.	Found
2.16	41.69	40.75	10.02	9.91
3.5	41.43	40.75	9.92	8.29
1.0	42.81	42.57	10.45	10.29
2.0	42.24	41.77	10.20	10.02
2.7	41.07	40.83	10.16	9.59
1.0	37.41	37.54	9.14	9.33
1.62	35.88	35.28	8.69	8.58
1.0	33.09	32.99	8.08	8.01
		33.35		8.12
1.9	30.47	30.15	7.36	7.29
1.0	49.26	49.58	11.03	11.15
2.07	51.13	50.09	10.90	10.78
1.0	44.67	44.59	10.62	10.59
1.58	44.75	43.29	10.54	10.16
2.75	44.82	43.62	10.37	9.97
	n 2.16 3.5 1.0 2.0 2.7 1.0 1.62 1.0 1.9 1.0 2.07 1.0 1.58 2.75	$\begin{array}{c cccc} n & & & & & & & & & & & & & & & & & & $	$\begin{array}{c c} & Carbon, \ \%\\ Calc. & Found \\ \hline 2.16 & 41.69 & 40.75 \\ \hline 3.5 & 41.43 & 40.75 \\ \hline 1.0 & 42.81 & 42.57 \\ \hline 2.0 & 42.24 & 41.77 \\ \hline 2.7 & 41.07 & 40.83 \\ \hline 1.0 & 37.41 & 37.54 \\ \hline 1.62 & 35.88 & 35.28 \\ \hline 1.0 & 33.09 & 32.99 \\ & & & & & & & \\ \hline & & & & & & \\ 1.9 & 30.47 & 30.15 \\ \hline 1.0 & 49.26 & 49.58 \\ \hline 2.07 & 51.13 & 50.09 \\ \hline 1.0 & 44.67 & 44.59 \\ \hline 1.58 & 44.75 & 43.29 \\ \hline 2.75 & 44.82 & 43.62 \\ \hline \end{array}$	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$

It is to be noted that molecular weight determinations corroborate the analytical data.

molecular weight value of the higher neopentyl-substituted siloxane also cannot be considered completely reliable since its infrared spectrum indicates the presence of uncondensed silanol groups. Because of the small amount of material available, no attempts to obtain complete condensation could be made.

DS WITH LYCLIC [(LT13)2010]4	Approximate ^a composition	$Me_{3}SiOSi(Me)(R)O[Si(Me)_{2}O]_{4.9}SiMe_{3}$	$Me_{3}SiOSi(Me)(R)O[Si(Me)_{2}O]_{5.6}SiMe_{3}$	$Me_{s}SiOSi(Me)(R)O[Si(Me)_{2}O]_{7.8}SiMe_{s}$	$Me_{3}SiOSi(Me)(R)O[Si(Me)_{2}O]_{8^{-2}SiMe_{3}}$	$\mathrm{Me}_{\mathrm{s}}\mathrm{SiOSi}(\mathrm{Me})(\mathrm{R})\mathrm{O}[\mathrm{Si}(\mathrm{Me})_{2}\mathrm{O}]_{\mathrm{5},\mathrm{s}}\mathrm{SiMe}_{\mathrm{s}}$
13/3 COMPOUN	Hydrogen, %	8.93	7.76	7.45	8.91	9.52
un)ren(u)	$\operatorname{Carbon}_{\%}$	35.36	31.60	30.35	39.51	39.65
	Mol. wt.	671	266	974	906	738
or (cui	d_4^{25}	0.945	1.051	1.110	0.930	0.925
DULLBRATION	$n_{ m D}^{25}$	1.4163	1.4268	1.4332	1.4101	1.4223
FRODUCTS OF	Я	(CH ₃) ₃ SiCH ₂	(CH ₃) ₃ GeCH ₂	(CH ₃) ₃ SnCH ₂	(CH ₃) ₃ CCH ₂	$(CH_3)_3SiC_2H_4$

(CH_a).SiOSi(CH_a)(R)OSi(CH_a). Comparing with Cverte [(CH_a),SiO]. Ę D₂₁ P C DaAnt

TABLE III

^a Calculated from molecular weights. The assumption is made that there is only one R group per molecule, *i.e.*, that the equilibration was:

 $\longrightarrow Me_{3}SiOSi(Me)(R)O[Si(Me)_{2}O]_{4z}SiMe_{3}$ $Me_{s}SiOSi(Me)(R)OSiMe_{s} + x(Me_{s}SiO)_{4}$

TABLE IV

VISCOSITY MEASUREMENTS OF SILOXANES (CH3)3SiO[Si(CH3)(R)O]Si(CH3)3

R	n	Temp., °C.	Viscosity, centistokes	E _{visc., cal.}
(CH ₃) ₃ SiCH ₂	1	0	3.19	
(,)		25	2.07	2735
		99.9	0.834	
(CH ₃) ₃ SiCH ₂	2.16	0	10.29	
(25.2	5.48	3680
		100.3	1.66	
(CH ₃) ₃ SiCH ₂	2.7	0	45.97	
		26.4	15.75	5171
		99.9	2.60	
(CH ₃) ₃ SiCH ₂	3.5	0	48.93	
		26.7	19.17	5198
		100.3	3.85	
(CH ₃) ₃ GeCH ₂	1	0	. 3.69	
		25	2.14	3050
		100	0.787	
(CH ₃) ₃ GeCH ₂	1.62	0	8.12	
		25	4.22	3678
		100.2	1.30	
(CH ₃) ₃ SnCH ₂	1	0	3.72	
		25	2.21	3061
		100	0.831	
(CH ₃) ₃ SnCH ₂	1.9	0	9.42	
		25	4.88	3736
		100	1.47	
$(CH_3)_3CCH_2$	1	0	3.33	
		25	2.12	2829
		100	0.830	
$(CH_3)_3CCH_2$	2.07	0	15.5	
		25	6.74	4327^{a}
		100	1.67	
$(CH_3)_3SiCH_2CH_2$	1	0	6.55	
		25	3.38	3963
		100	0.918	
$(CH_3)_3SiCH_2CH_2$	1.58	0	19.39	
		25	7.61	5240
		100	1.41	
(CH ₃) ₃ SiCH ₂ CH ₂	2.75	0	111.1	
		25	28.13	7340
C11.4		100	2.86	
CH ₃ °	1			2230
	2	^	a	2510
CICH ₂ "	1	0	2.46	
CICIT 4		99.4	0.70	2554
CICH2"	2	0	6.02	0077
		99.4	1.18	3311

^a Viscosity data on methyl siloxanes from M. J. Hunter, E. L. Warrick, J. F. Hyde, and C. C. Currie, J. Am. Chem. Soc., 68, 2284 (1946); on chloromethylsiloxanes from J. L. Speier, *ibid.*, 71, 273 (1949).

Considering first the MDM compounds, it can be seen from Table IV that the $E_{\text{visc.}}$ values increase as follows:

$\mathrm{CH}_3 < \mathrm{CiCH}_2 < \mathrm{Me}_3\mathrm{SiCH}_2 < \mathrm{Me}_3\mathrm{CCH}_2 < \mathrm{Me}_3\mathrm{GeCH}_2 = \mathrm{Me}_3\mathrm{SnCH}_2 < \mathrm{Me}_3\mathrm{SiCH}_2\mathrm{CH}_2$

It would appear that there is only a small increase in the intermolecular attraction when an organic group (i.e., the neopentyl group) is replaced by an organometallic group of similar structure. The higher $E_{\text{visc.}}$ values of the trimethylgermyl- and trimethylstannyl-substituted siloxanes may indeed be due to dipole-dipole interactions of the polar metal-carbon links between adjacent chains, but if this is so one would expect the trimethylsilylmethylsubstituted siloxanes to have a higher $E_{\rm visc.}$ value than the neopentylsubstituted siloxanes. However, consideration of Fischer-Hirshfelder models of these two siloxanes shows that rotation about the Si-O axis is more restricted in the latter than in the trimethylsilylmethyl-substituted siloxane. Therefore, an explanation for the higher $E_{\text{visc.}}$ value and for the higher actual viscosity of the neopentylsiloxane may be sought in the decreased "siloxane-like" character of this compound due to restriction of the rotation about the Si-O axis. Such motion, first postulated by Roth and Harker,¹⁸ has been used to explain some of the remarkable properties of the polysiloxanes, including the low $E_{\text{vise.}}$ values of the methylpolysiloxanes.

More recently nuclear magnetic resonance absorption studies^{19,20} have shown that there is also considerable motion about the Si-C bond in methylsiloxanes even at very low temperatures where all motion in organic compounds is frozen out. Preliminary nuclear magnetic resonance absorption studies²¹ confirm that there is considerably less motion in the neopentyl-substituted MDM compound reported here, while in the case of the trimethylstannylmethyl-substituted siloxane there appears to be no such drastic restriction of motion. Whether this less restricted motion in the Me_3MCH_2 -substituted siloxanes (M, is Si, Ge Sn) is due to decreased steric interference or to some other cause must remain an open question at this time. In any case this freer motion may well compensate for any increased polar effects as one goes down the group Si, Ge, Sn, with the result that only small differences in the $E_{\text{vise.}}$ values and in the actual viscosities are observed. The higher energies of activation of viscous flow and the higher actual viscosities of the Me₃MCH₂-substituted siloxanes when compared with those of the chloromethyl-substituted siloxanes may possibly be explained by more restricted rotation about the Si-O axis in the former, since the C-Cl bond in the latter is only slightly less polar than the C-Si, C-Ge and C-Sn bonds and is not surrounded by bulky methyl groups.

Steric interference between different molecules may also be possible and contribute to the higher $E_{\text{visc.}}$ values, but in the MDM compounds such effects should not be important except in the case of the β -trimethylsilylethyl-substituted siloxane. Here the interference with intramolecular rotation should be less marked because the highly branched group is farther out, but intermolecular interference may be greater because of the same reason.

In the higher siloxanes it is apparent that the presence of several highly branched organometallic substituents leads to a rapid increase in the actual viscosity and the energy activation of viscous flow. Again the two opposite effects, intermolecular dipole interaction and restricted rotation about the Si—C and Si—O bonds (possibly caused by steric hindrance of the bulky substituents), may serve to explain these increases. The latter influence is probably the more important.

EXPERIMENTAL

(1) Materials

The starting silanes have previously been described.¹¹ Hexamethyldisiloxane (pure grade) was obtained from Dow Corning Corporation, and octamethylcyclotetrasiloxane from the Silicone Products Department, General Electric Company. Carbon and hydrogen analyses were carried out by Dr. S. M. Nagy and his associates, Microchemical Laboratory, Massachusetts Institute of Technology, and the active hydrogen determinations by Schwarzkopf Microanalytical Laboratories, Woodside, New York.

(2) Hydrolyses

Method A. The hydrolysis of methyl- β -trimethylsilylethyldichlorosilane is described as an example.

A mixture of 100 ml. of ether and 100 ml. of distilled water was cooled to 5° and 50 g. (0.231 mole) of methyl- β -trimethylsilylethyldichlorosilane was added slowly with vigorous stirring while the temperature was maintained at 5° . After the addition had been completed the reaction mixture was allowed to warm up to room temperature and was then stirred vigorously for 10 hours. Subsequently the organic layer was separated, washed several times with distilled water, and dried over anhydrous sodium sulfate. After distillation of the ether at atmospheric pressure the residue was fractionated at reduced pressure through an 18-inch Vigreaux column. A 71% yield of volatiles, 26.2 g. of liquid boiling from 141° at 0.2 mm. to 183° at 0.3 mm., was obtained. A heavy viscous residue remained in the still pot. Refractionation gave the fractions listed in Table I. That the fraction boiling at 138–142° at 0.175 mm. was relatively pure trimer was shown by: (a) the strong band in its infrared absorption spectrum at 9.9 μ , which is indicative of the cyclic trimer structure, and the absence of a strong band at 9.3 μ , which would indicate the presence of tetrameric or higher cyclics²²; (b) the fair agreement of the observed molar refraction using the calculated molecular weight of the trimer in the Lorentz equation with the molar refraction calculated from the bond refraction values of Vogel et al.²³ (found: 140.50; calc. 141.37); and (c) the determination of the molecular weight by the cryoscopic method in cyclohexane solution.

Method B. The hydrolysis of methyl(trimethylsilylmethyl)dimethoxysilane is given as an example.

Methyl(trimethylsilylmethyl)dimethoxysilane, 70 g. (0.364 mole) was added slowly with vigorous stirring to a mixture of 250 ml. of ether and 250 ml. of distilled water to which three drops of concentrated hydrochloric acid had been added. After the mixture had been stirred for 12 hours, the ether layer was separated and dried and the ether distilled off. The residue was then distilled and four fractious were taken: (1) 15.4 g., b.p. 108–127° at 0.1 mm.; (2) 10.5 g., b.p. 127–132° at 0.1 mm.; (3) 10.0 g., b.p., 140–170° at 0.1 mm.; (4) 4.5 g., b.p. 170° at 0.1 mm.

The infrared spectra of these fractions, taken in carbon disulfide solution, indicated that fractions (1) and (2) contained OH groups, while fractions (3) and (4) did not. Fractions (1) and (2) began to crystallize after they had stood for four days. Attempted recrystallization from methanol or from $20-40^{\circ}$ petroleum ether at low temperatures was unsuccessful. Only oils could be obtained; these, when seeded with a crystal of the original material crystallized on standing overnight in an ice box. The crystals were then washed with a small amount of cold petroleum ether and squeezed dry under water pump suction with a rubber dam. The crystalline product reacted only slowly with Karl Fischer reagent, making the detection of the endpoint difficult, but the substance appeared to be a silanol and probably bis-(trimethylsilylmethyl)dimethyl-1,3-disiloxanediol. Determinations of molecular weight in cyclohexane gave values larger than that expected for the diol. However it has been $shown^{24}$ that trimethylsilanol and triethylsilanol are associated in cyclohexane solution. For trimethylsilanol the association factor $MW_{found}/MW_{calc.}$ varied from 1.78 at a concentration of 0.0151 molal to 3.28 for a 0.1450 molal solution. In the disiloxanediol described above the association factor was found to be 3.09 at a concentration of 0.0443 molal and 3.22 for a 0.0766 molal solution. It is not surprising that a disiloxanediol exhibits such high association.

The same bis(trimethylsilylmethyl)dimethyl-1,3-disiloxanediol was condensed to the cyclic trisiloxane by refluxing in the presence of dry aluminum oxide at 10 mm. pressure and then distilling at lower pressure. No OH absorption at 3 μ was observed in the infrared spectrum of the distillate, and no band indicative of tetramer at 9.3 μ appeared.

ANALYSIS: Calcd. for $(Me_3SiCH_2(Me)SiO)_3$: C, 41.05; H, 9.65; MW, 439. Found: C, 40.72; H, 9.65; M.W., 446; n_{D}^{25} , 1.4400, d_{2}^{45} , 0.921.

When this method was used to hydrolyze methylneopentyldimethoxysilane, removal of the ether from the organic layer of the hydrolysis mixture gave a heavy oil that formed a crystal slush on cooling. This was filtered under suction to yield 55.3 g. of a waxy white solid which was then washed with cold $20-40^{\circ}$ petroleum ether and filtered again. The crystals so obtained were in the form of glistening white flakes. Their infrared spectrum in chloroform solution indicated that uncondensed silanol groups were present. A portion of the crystalline product was recrystallized from a mixture of chloroform and $30-60^{\circ}$ petroleum ether and dried *in vacuo* to yield material melting 98.0–98.8° (uncorr.), which was identified as methyl-neopentylsilanediol.

The other hydrolyses are summarized in Table I.

Hydrolysis of Trimethylsilylmethyldimethylmethoxysilane. To 29 g. of this silane in a 250 ml. three-necked flask equipped with a stirrer, reflux condenser, and a dropping funnel, 20 ml. of concentrated sulfuric acid was slowly added. The mixture became quite hot during the addition; it was subsequently stirred for 15 hours at room temperature. A homogeneous system resulted. The reaction mixture was then poured into 500 ml. of distilled water; the organic layer was separated, washed three times with water, three times with a saturated solution of sodium bicarbonate, and finally again with water, and was dried over Drierite. Fractional distillation gave 13.5 g. of 1,3-bis(trimethylsilylmethyl)tetramethyldisiloxane, b.p. 84° at 0.7 mm. to 88° at 0.95 mm., a yield of 55%.

(3) Equilibrations

Sulfuric Acid-Catalyzed Equilibration. A mixture of 257.1 g. of (a)hexamethyldisiloxane, 34.5 g. of a mixture of 1.3-bis(trimethylsilylmethyl)dimethyl-1,3-disiloxanediol and methyl(trimethylsilylmethyl)cyclosiloxanes and 3.4 ml. of concentrated sulfuric acid was stirred at room temperature The sulfuric acid remained as a separate layer throughout for 17 hours. After this period of stirring, 25 ml. of distilled water was this treatment. added and stirring was continued for 15 minutes. The organic layer was then separated, washed with 5% sodium bicarbonate solution and with distilled water, and dried over Drierite. Fractional distillation of the organic layer gave 205 g. of hexamethyldisiloxane, 5 g. of liquid boiling from 75° at 2.5 mm. to 90° at 0.1 mm., 14.4 g. of liquid boiling from 90 to 105° at 0.1 mm. and a higher-boiling residue weighing 25.5 g. The infrared absorption spectra of the 90-105° fraction and of the residue indicated that some cyclic material was still present.

(b) Potassium Hydroxide-Catalyzed Equilibrations. All potassium hydroxide-catalyzed equilibrations were carried out in the following manner: A mixture of a hydrolysis product of Table I with hexamethyldisiloxane isopropyl alcohol, and potassium hydroxide dissolved in a small amount of water was heated under reflux for 12 to 20 hours in a one-liter, three-necked flask equipped with a Hirschberg stirrer, a reflux condenser, and a thermometer. After the reaction mixture had cooled to room temperature it was washed with three 75 ml. portions of saturated ammonium chloride solution, dried over potassium carbonate, and fractionally distilled. The excess hexamethyldisiloxane and isopropyl alcohol were distilled at atmospheric pressure in some cases, at reduced pressure in others. The residue was fractionated at reduced pressure. The experimental data are listed in Table V.

In the case of the MDM-octamethylcyclotetrasiloxane equilibrations the same procedure was followed with the following slight modifications;

Hydrolysis product	Wt., g.	[(CH ₃) ₃ Si] ₂ O Wt., g.	Iso-C ₃ H ₇ OH Vol., ml.	KOH Wt., g.	H2O Vol., ml.	Reflux time, hr.	Products, wt., g.
Cyclic [(CH ₃) ₃ SiCH ₂ (CH ₃)SiO] _x	51	202.5	200	40	35	20	MDM, 43 MD ₂ M, 6 MD M 0 5
Mixt. of cyclic {(CII ₃) ₃ GeCH ₂ (CH ₃)SiO] _x	27.5	50	100	21	18	12.5	MDM, 22.3 MDM, 22.3 MD,M 0.8
Mixt. of cyclic [(CH ₃) ₃ SnCH ₂ (CH ₃)SiO] _x and siloxonodial	34.3	81.2	100	21	18	13	MDM, 37.8 MDM, 37.8 MD, M 9.8
(CH ₃) ₃ CCH ₂ (CH ₃)Si(OH) ₂	26.9	60	100	20	18	12.5	MDM, 22.6
Cyclic [(CII ₃) ₈ SiC ₂ H ₄ (CH ₃)SiO] _z	29.4	50	100	20	18	12	MDM, 18.0 MDM, 18.0 MD ₁₋₅₈ M, 10.0
							MD ₂₋₇₅ M, 9.3

TABLE V

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ΓAB

Potassium Hydroxide-Catalyzed Equilibration of (CH₃)₃SiOSi(CH₃)(R)OSi(CH₃)₃ Compounds with Cyclic [(CH₃)₂SiO₄]

			5	1 5 ~ - ~ Z / e					
В	(CH _a) _s SiOSi(CI Wt., g.	H ₃)(R)OSi(CH ₃) ₈ Molea	[(CH ₃] Wt., g.	2SiO1 Moles	Iso-C ₃ H ₇ OH Vol., ml.	KOII Wt., g.	H2O Vol., ml.	Reflux time, hr.	Residue wt., g.
(CH ₃) ₃ SiCH ₂	28.5	0.092	27.5	0.092	100	20	18	10	24.5
(CH ₃) ₃ GeCH ₂	13.1	0.037	11.0	0.037	60	10	8	10.5	10.0
(CH ₃) ₃ SnCH ₂	21.0	0.053	15.6	0.053	80	15	13	10	15.4
(CH ₃) ₃ CCH ₂	19.7	0.067	20.0	0.067	80	18	15	10	20.0
(CH _a) _a SiC _a H,	12.0	0.027	8.0	0.027	40	2	9	10.5	10.0

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after removal of the isopropyl alcohol the residue was filtered and the lower boiling siloxanes were then removed by distillation at reduced pressure (0.1 to 0.5 mm.). No boiling chips were used. The distillation flask was heated to 200° on all cases. The residue that remained was used for the viscosity determinations. Experimental data are given in Table VI and viscosity data in Table VII.

TABLE VII

VISCOSITY MEASUREMENTS OF MDM-D4 EQUILIBRATION PRODUCTS

		Vised	sitv	
R	Mol. wt.	Cs.	At °C.	Evise., cal.
(CH ₃) ₃ SiCH ₂	671	62.48	0	
		20.17	25	6271
		2.20	100	
(CH ₃) ₃ GeCH ₂	766	93.73	0	
		26.72	25	7192
		2.45	100	
$(CH_3)_3SnCH_2$	974	44.37	0	
		17.00	25	5418
		3.14	100	
$(CH_3)_3CCH_2$	900	33.91	0	
. ,		16.01	25	4301
		3.99	100	
$(CH_3)_3SiC_2H_4$	738	91.59	0	
		26.62	25	6664
		3.28	100	

(4) Viscosity Determinations

Fenske viscometer tubes, Exax blue line, conforming to the specifications of The American Society for Testing Materials,²⁵ were used in this study. The viscometers were calibrated using pure methylsiloxanes of known viscosity at a given temperature. The method described in reference (25) was used in the viscosity determinations.

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Synopsis

In an attempt to increase the intermolecular attraction between polyorganosiloxane chains and rings, polar groups have been introduced into methyl groups attached to the silicon atoms. To avoid the usual weakening of the C—Si bond by negative polar substituents, positive substituents of the type $(CH_3)_3M$ (where M is Si, Ge, or Sn) were employed in this study. Cyclic trimers and extended linear polymers were prepared, both from the pure polar-substituted monomers and from mixtures of these monomers with octamethyltetrasiloxane. Intermolecular attraction was estimated by measuring viscosities and activation energies of viscous flow. The preparations also were compared in these respects with pure dimethylsiloxanes and with neopentylsiloxanes. The results show that intermolecular attraction is increased by the positive polar substituents, and that the C-Si bond is rendered more stable toward OII- attack by such positive substituents than by negative. More detailed analysis indicates that the effects of the groups on the viscosity of the polymers depends on: (1) the dipole attraction of the polar groups, (2) the bulk or steric effect of the enlarged group, and (3) the effect of the metal M upon the ease of rotation of the methyl groups (the characteristically free intramolecular motion of silicon polymers). The trends of these effects oppose each other in the C-Si-Ge-Sn series, and so limit the observed increase of viscosity.

Résumé

En vue d'augmenter l'attraction intermoléculaire des chaînes et anneaux des polysiloxanes organiques, on a introduit des groupes polaires dans les groupes méthyliques attachés aux atomes de silicium. En vue d'éviter le relâchement habituel de la liaison C—Si par l'introduction de substituants polaires négatifs, on a utilisé dans cette étude l'introduction de groupes positifs du type $(CH_3)_3M$ (où M est Si, Ge ou Sn). Des trimères cycliques et des polymères linéaires étendus ont été préparés, tous deux aus dépens de monomères purs substitués et au départ de mélanges de ces monomères avec la octaméthyltétrasiloxane. L'attraction intermoléculaire a été estimée par des mesures de viscosités et d'énergies d'activation d'écoulement visqueux. Les préparations ont également été comparées avec les diméthylsiloxanes pures et les néopentylsiloxanes. Les résultats montrent que l'attraction intermoléculaire *est* accrue par les substituants positifs, et que le lien C—Si est rendu plus stable à l'égard d'une attaque par OH^- par ces substituants positifs que par des substituants négatifs. Une analyse plus détaillée montre que les effets des groupes sur la viscosité des polymères dépendent: (1) de l'attraction dipolaire des groupes polaires, (2) la grosseur ou l'effet stérigue de la groupe augmentée, et (3) de l'effet du métal M sur la possibilité de rotation des groupes méthyliques (mobilité intramoléculaire considérable, caractéristique des polymères siliconiques). Ces effets s'opposent les uns aux autres dans les séries C-Si-Ge-Sn, et limitent ainsi les augmentations de viscosité.

Zusammenfassung

In einem Versuch, die intermolekulare Anziehung zwischen Polyorganosiloxan-Ketten und -Ringen zu erhöhen, wurden polare Gruppen in Methylgruppen eingeführt, die an Silizium-Atome gebunden sind. Um die übliche Schwächung der C-Si-Bindung bei negativen polaren Substituenten zu verhindern wurden positive Substituenten vom Typus (CH₃)₃M (wo M Si, Ge oder Sn ist) in dieser Untersuchung verwendet. Es wurden cyclische Trimere und ausgedehnte lineare Polymere hergestellt, sowohl aus den reinen polar-substituierten Monomeren als auch aus Mischungen dieser Monomere mit Octamethyltetrasiloxan. Die intermolekulare Anziehung wurde durch Messung der Viskositäten und Aktivationsenergien des viskosen Fliessens abgeschätzt. Die Produkte wurden auch in dieser Hinsicht mit reinen Dimethylsiloxanen und mit Neopentylsiloxan verglichen. Die Resultate zeigen, dass die intermolekulare Attraktion durch die positiven polaren Substituenten erhöht wird, und dass die C-Si-Bindung gegen OH⁻-Angriff durch solche positiven Substituenten beständiger als durch negative gemacht wird. Genauere Analyse zeigt, dass die Einwirkungen der Gruppen auf die Viskosität der Polymere abhängig ist von: (1) der Dipolanziehung der polaren Gruppen, (2) der Massen-oder sterischen Wirkung der vergrösserten Gruppen und (3) der Einwirkung des Metals M auf die Leichtigkeit der Rotation der Methylgruppen (die charakteristisch freie intramolekulare Bewegung von Silikonpolymeren). Die Richtungen dieser Einwirkungen stehen in der C-Si-Ge-Sn-Reihe gegeneinander und beschränken so die beobachtete Erhöhung der Viskosität.

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