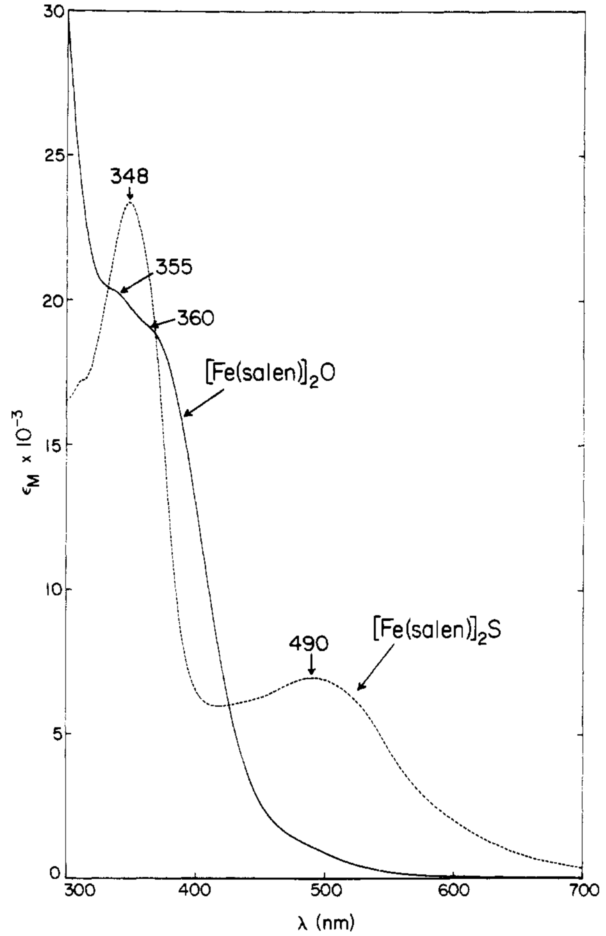

Figure 4. Absorption spectra of $[Fe(salen)]_2S$ and $[Fe(salen)]_2O$ in DMF solutions in the UV-visible region. [λ_{max}, nm (ϵ_M)]: 490 (6930), 348 (23 500); 360 (19 200), 355 (20 400).

Possible Biological Relevance. Aquomet-Hr and H_2S or sulfide at pH ~8 form a species, sulfide-Hr, with the composition 2 Fe:S^{2-}.[47,48] Sulfide-Hr is a chromophore with a band at 510 nm (ϵ_M ~1200), suggesting, as previouisly recognized,[47] a relationship with $[Fe(salen)]_2S$ and $[Fe(HEDTA)]_2S^{2-}$. Recent work[48] has shown that sulfide-Hr is stabilized in the mixed-valence Fe(III) ($S = {}^5/_2$) + Fe(II) ($S = 2$) oxidation level, which is spin coupled to give a $S = {}^1/_2$ ground state. Valence states are trapped on the Mössbauer time scale. Consequently, the Fe_2S portions of sulfide-Hr and $[Fe(salen)]_2S$ are not isoelectronic. However, in DMF solution $[Fe(salen)]_2S$ undergoes a well-defined electrochemical reduction at $E_{1/2} = -1.27$ V vs. SCE ($\Delta E_p = 80$ mV, $i_{p,c}/i_{p,a} \cong 1$). The corresponding reduction of $[Fe(salen)]_2O$ in DMF occurs at -1.07 V. In Me_2SO solution the potential is -1.05 V.[49] $[Fe(salen)]_2S$ also exhibits a one-electron oxidation in DMF at -0.28 mV ($\Delta E_p = 90$ mV, $i_{p,c}/i_{p,a} \cong 1$). $[Fe(salen)]_2O$ is reported to afford only poorly resolved electrochemical oxidation, but its diiron(III,IV) level has been reached by chemical oxidation and isolated.[9] These observations raise the possibility of isolating or generating the species $[Fe(salen)]_2S^{+,-}$, with the anion being isoelectronic with the currently characterized state of sulfide-Hr. For the latter, available evidence does not permit a distinction between the proposed[47] structures $Fe-S^{2-}-Fe$ and $Fe\cdots Fe-S^{2-}$. Such a distinction may be possible upon elucidation of the properties of $[Fe(salen)]_2S^-$.

In summary, this research provides characterization of the only structurally authenticated example of the Fe(III)-S-Fe(III) single bridge. The set $[Fe(salen)]_2S^{-,0,+}$ (stability permitting) provides an attractive opportunity for further study of structural and electronic properties mediated by a sulfide bridge, including trapped vs. delocalized valence states and magnetic coupling.

Acknowledgment. This research was supported by NIH Grant GM 28856. NMR and X-ray diffraction equipment were obtained by NSF Grants CHE 80-00670 and CHE 80-08891.

Supplementary Material Available: Listings of anisotropic temperature factors, calculated hydrogen atom positions, magnetic susceptibility data (22-291 K), and observed and calculated structure factors for $[Fe(salen)]_2S$ (21 pages). Ordering information is given on any current masthead page.

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Linear Polysiloxanes from Dichlorosilane

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Received June 19, 1984

Polysiloxanes of type $RR'R''SiO(SiH_2O)_nSiRR'R''$ (R, R', R'' = Me, Me, Me; Me, H, H; Et, Et, Et; Me, Me, H) have been prepared by three different methods: (1) reactions of $ClSiH_2O(SiH_2O)_nSiH_2Cl$ with CH_3MgBr, Me_3SiOH, and Et_3SiOH; (2) H_2SO_4-catalyzed equilibration of cyclic $[H_2SiO]_n$ oligomers with $Me_3SiOSiMe_3$; (3) cohydrolysis of H_2SiCl_2 with Me_3SiCl and Me_2HSiCl using NaH_2PO_4/Na_2HPO_4-buffered media. Lower species, $Me_2RSiO(SiH_2O)_nSiMe_2R$ (n = 1-3), were isolated and characterized (R = Me, H).

Introduction

In an earlier paper[2] we described the cyclic polysiloxanes, $[H_2SiO]_n$, which are obtained when dichlorosilane, H_2SiCl_2, is hydrolyzed under the appropriate conditions.[3] Also of interest to us were linear siloxanes of the type $RR'R''SiO[SiH_2O]_nSiRR'R''$, where R, R', and R'' can be the same or different. We report here our studies directed toward this goal. Linear polysiloxanes containing H_2SiO units in the polysiloxane chain have been reported in the patent literature.

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(2) Seyferth, D.; Prud'homme, C. C.; Wiseman, G. H. *Inorg. Chem.* **1983**, *22*, 2163.
(3) Previous studies of the hydrolysis of dichlorosilane are discussed in ref 2.

0020-1669/84/1323-4412$01.50/0

Table I. Cohydrolysis of Dichlorosilane and Trimethylchlorosilane

amt of Me_3SiCl, mmol	amt of H_2SiCl_2, mmol	Me_3SiCl/ H_2SiCl_2	siloxane yield, %	n^a	amt of siloxanes, mmol (wt %)
664	166	4	90	0	189 (55.5)
				1	78 (29.2)
				2	20 (9.4)
				3	2.9 (1.6)
				4	<0.1 (<0.5)
486	243	2	91.4	0	84 (29.3)
				1	97 (43.4)
				2	37 (20.2)
				3	10 (6.5)
				4	2 (1.5)
323	323	1	92.6	0	17 (7.25)
				1	54 (29.7)
				2	36 (23.9)
				3	14 (11.0)
				4	5.5 (5.0)
203	405	0.5	87.5	0	10.1 (5.4)
				1	19 (12.7)
				2	18 (14.8)
				3	13.5 (13.2)
				4	9.2 (10.4)

[a] For $Me_3SiO[SiH_2O]_nSiMe_3$.

They have been prepared by the cohydrolysis of trimethylchlorosilane and dichlorosilane in cold, concentrated hydrochloric acid.[4,5] The sulfuric acid catalyzed equilibration of the mixed cyclic siloxanes obtained by cohydrolysis of H_2SiCl_2 and Me_2SiCl_2 with hexamethyldisiloxane gave polysiloxanes of type $Me_3SiO[SiH_2O]_a[Me_2SiO]_bSiMe_3$.[6] However, individual polysiloxanes were not isolated and characterized. The products only were described as oils of a given viscosity and base-hydrolyzable hydrogen content. Thus, further investigations using currently available methods such as gas chromatography (GLC) and ^1H and ^{29}Si NMR spectroscopy seemed worthwhile.

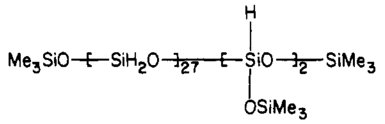
Results and Discussion

The hydrolysis of dichlorosilane at about −40 to −50 °C in an organic solvent such as diethyl ether, dichloromethane, or pentane with a slight deficiency of water gave chlorine end-blocked linear siloxanes, $ClSiH_2O[SiH_2O]_nSiH_2Cl$, as well as cyclic polysiloxanes, $[H_2SiO]_n$. For example, in one such experiment, carried out in diethyl ether, the organic layer was distilled to remove solvent and the volatile cyclic $[H_2SiO]_n$ oligomers, leaving behind a 54% yield of a clear, colorless, slightly viscous oil. The 60-MHz proton NMR spectrum of this oil showed two singlets at δ 4.68 and 5.14, due to internal SiH_2O units and terminal $ClSiH_2O$ groups, respectively. The integrated ratio of these signals led to an *average* constitution of $ClSiH_2O[SiH_2O]_{23}SiH_2Cl$. (The product, no doubt, is composed of a mixture of polymeric species of differing chain length; the molecular weight determination by integration of the ^1H NMR spectrum (internal SiH_2 vs. terminal SiH_2Cl groups) gives the SiH_2/SiH_2Cl ratio, which can be translated into an *average* chain length, $\bar{n}$.) The results of a combustion analysis of this product were in fairly good agreement with this formulation. Quite possibly, the nonvolatile product contained some larger $[H_2SiO]_m$ cyclics, but as the yield of the respective oligomers decreased rapidly with increasing m,[2] their concentration in the product very likely was quite low.

The ^{29}Si NMR spectrum of the product oil showed three triplets at δ_{Si} −30.2, −47.8, and −49.0, with $J(Si\text{–}H) = 277.6$, 260.7, and 257.4 Hz, respectively. These may be assigned to the $Cl\mathit{Si}H_2O$, the $ClSiH_2O\mathit{Si}H_2O$ and all of the rest of the internal SiH_2O units, respectively. (For comparison, δ_{Si} of $[H_2SiO]_5$ and of $[H_2SiO]_6$ and higher cyclic oligomers are −48.9 and −49.2, respectively.)[2]

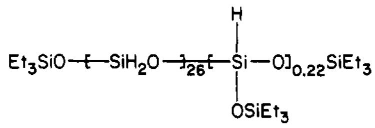
Low polymers of type $ClSiH_2O[SiH_2O]_nSiH_2Cl$ are of interest as potential intermediates for the preparation of silicone block copolymers, for instance, by their reaction with silicone polymers of type $HOSiMe_2O[SiMe_2O]_xSiMe_2OH$. However, we were also interested in converting the chlorine end-blocked polymers into species with less reactive terminal groups. The reactivity of the terminal Si–Cl bonds made this possible. One means of accomplishing this was with methylmagnesium bromide, but unless low temperatures and short reaction times were used, displacement of some hydrogen (as well as of chlorine) from silicon occurred. Thus, at about −50 °C the product of the reaction of CH_3MgBr with the chlorine end-blocked polymer was $CH_3SiH_2O[SiH_2O]_pSiH_2CH_3$, but a reaction at room temperature gave a polymer containing some internal $Si(CH_3)(H)O$ units as well. Even at low temperature, the methylation process was not straightforward. The yield of soluble product was not high and insoluble silicon-containing materials also were formed. Moverover, the isolated CH_3 end-blocked oil was of lower average molecular weight than the starting material. In one instance, such methylation of $ClSiH_2O[SiH_2O]_{23}SiH_2Cl$ at −50 °C gave $CH_3SiH_2O[SiH_2O]_{14}SiH_2CH_3$. The ^1H and ^{29}Si NMR spectra of this product, as well as the combustion analysis, were in excellent agreement with this formulation, with integration of the proton NMR spectrum (internal SiH_2 vs. terminal CH_3 groups) giving the average molecular weight.

Reactions with trialkylsilanols, R_3SiOH, converted $ClSiH_2O[SiH_2O]_nSiH_2Cl$ polymers to ones of type $R_3SiO[SiH_2O]_{n+2}SiR_3$. Thus, a reaction of $ClSiH_2O[SiH_2O]_{31}SiH_2Cl$ with trimethylsilanol in diethyl ether at room temperature gave a clear, slightly viscous oil in high yield whose ^1H and ^{29}Si NMR spectra indicated the constitution **1**; i.e., a small amount of attack by the silanol at the Si–H bond had occurred. When this reaction was repeated, initially at −50 °C, with slow warming to room temperature, ^1H NMR spectroscopy showed the virtual absence of contaminating $Si(OSiMe_3)(H)O$ units. Triethylsilanol reacted with $ClSiH_2O[SiH_2O]_{31}SiH_2Cl$ in diethyl ether at room temperature to give **2**, as determined by ^1H NMR.



$$Me_3SiO\text{—}[SiH_2O]_{27}\text{—}[\overset{H}{\underset{OSiMe_3}{Si}}O]_2\text{—}SiMe_3$$

1



$$Et_3SiO\text{—}[SiH_2O]_{26}[\overset{H}{\underset{OSiEt_3}{Si}}\text{—}O]_{0.22}SiEt_3$$

2

This approach to the preparation of linear $[SiH_2O]_n$ polymers with unreactive terminal groups did not seem very promising, and other routes were examined. The sulfuric acid catalyzed equilibration of cyclic $[H_2SiO]_m$ oligomers with hexamethyldisiloxane at 70 °C resulted in essentially complete disappearance of the cyclic siloxanes and formation of a mixture of linear $Me_3SiO[SiH_2O]_nSiMe_3$ species. A number of such experiments with different $SiH_2O/Me_3SiOSiMe_3$ ratios were carried out. The maximum value of this ratio subjected to experiment was 2.8, but use of higher ratios should

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[4] British Thomson-Houston Co., Ltd. British Patent 638 586, 1950; *Chem. Abstr.* **1950**, *44*, 8104.

[5] Wilcock, D. F.; Hurd, D. T. U.S. Patent 2 547 678, 1951; *Chem. Abstr.* **1951**, *45*, 8029.

[6] Bailey, D. L.; York, E. R. U.S. Patent 2 810 628, 1957; *Chem. Abstr.* **1958**, *52*, 1516; British Patent 788 983, 1958; *Chem. Abstr.* **1958**, *52*, 14652.

Table II. Equilibration of $[H_2SiO]_m$ with $Me_3SiOSiMe_3$ ($SiH_2O/Me_3SiOSiMe_3$ Molar Ratio 2.80)[a]

"n" in $Me_3SiO[SiH_2O]_nSiMe_3$	amt, mmol	mol % of total $Me_3SiO[SiH_2O]_nSiMe_3$
0	1.20	8.05
1	3.49	23.4
2	3.86	25.9
3	2.78	18.6
4	1.65	11.1
5	0.92	6.17
6	0.48	3.22
7	0.25	1.68
8	0.13	0.87

[a] Reaction of 14.2 mmol of $Me_3SiOSiMe_3$, 39.7 mmol of SiH_2O, 0.046 g of concentrated H_2SO_4, and 0.49 g of CH_2Cl_2 for 3 h at 70 °C.

give linear materials of higher molecular weight. (Note that the action of concentrated sulfuric acid on a neat mixture of cyclic $[H_2SiO]_m$ gave an elastomeric material.)[2] GLC analysis of the reaction mixture when the $SiH_2O/Me_3SiOSiMe_3$ ratio was 2.80 gave the composition shown in Table II. The species formed in these equilibration reactions appear to be less disperse than the random distribution as calculated from the Flory theory of random rearrangement as adapted to siloxane polymers by Carmichael and Heffel.[7] This could be due in part to inaccuracies in the data caused by the necessity of extrapolating GLC weight response factors past $Me_3SiO[SiH_2O]_2SiMe_3$. However, the major part of the deviation very likely is due to the fact that the standard free energy of a siloxane linkage in a very short linear chain is different from the free energy of an isolated siloxane linkage in a longer chain.

Finally, another potential route to linear polysiloxanes of the type $R_3SiO[SiH_2O]_nSiR_3$ is the cohydrolysis of H_2SiCl_2 with a monochlorosilane, R_3SiCl.[4,5] In our first experiments, a large excess of water was added to a solution of dichlorosilane and 2 mol equiv of trimethyl- or dimethylchlorosilane in diethyl ether at 0–10 °C. Isolation by GLC and characterization of the major products soon showed that these were not the right reaction conditions. Substantial amounts of products in which a Si–H function had been replaced by a $SiOSiMe_3$ or $SiOSiMe_2H$ function were present. Thus, in such an experiment in which trimethylchlorosilane was used as the end-blocking reagent the following products were obtained in the weight percent of total hydrolysate indicated: $Me_3SiOSiMe_3$ (24); $Me_3SiOSiH_2OSiMe_3$ (25); $Me_3SiO[SiH_2O]_2SiMe_3$ (7.5); $Me_3SiO[SiH_2O]_3SiMe_3$ (<1); $[Me_3SiO]_3SiH$ (12); $[Me_3SiO]_2Si(H)OSiH_2OSiMe_3$ (14). Without doubt, it is the hydrochloric acid formed in the hydrolysis reaction that is responsible for the reaction at the Si–H bonds, since the SiH function is well-known to be subject to acid-catalyzed hydrolysis.[8] In order to avoid acid-induced Si–H hydrolysis, the cohydrolysis of H_2SiCl_2 with Me_3SiCl and Me_2HSiCl was carried out with a 1:1 NaH_2PO_4/Na_2HPO_4 pH 7 buffer system. This approach was successful, and best results were obtained when a cold solution of the chlorosilanes in diethyl ether was added to a large excess of the cold (0–5 °C) aqueous buffer solution. Application of this procedure to the cohydrolysis of a 2:1 (molar) mixture of Me_3SiCl and H_2SiCl_2 gave $Me_3SiOSiMe_3$ (44), $Me_3SiOSiH_2OSiMe_3$ (28), $Me_3SiO[SiH_2O]_2SiMe_3$ (18), $Me_3SiO[SiH_2O]_3SiMe_3$ (7.5), and none of the products derived from attack at Si–H.[9] This approach was equally successful in the cohydrolysis of Me_2HSiCl/H_2SiCl_2 mixtures.

With a useful procedure for the cohydrolysis of dichlorosilane in hand, we carried out some experiments in which the Me_3SiCl/H_2SiCl_2 ratio was varied. The results are given in Table I. No significant amounts of cyclic $[H_2SiO]_m$ products were observed in these experiments. Traces of unidentified products were found in the cohydrolysis of Me_3SiCl and H_2SiCl_2 in 1:2 ratio, and these might have been cyclic $[H_2SiO]_m$ species. The yields of hydrolysate obtained in these experiments (after water wash of the ether layer and removal of solvent) were 90% or better. As expected, the percentage of volatile products in the hydrolysate, $Me_3SiO[SiH_2O]_nSiMe_3$ (n = 0–4), decreased as the Me_3SiCl/H_2SiCl_2 ratio was decreased, and larger amounts of higher molecular weight material (n > 4) were formed. Thus, use of still lower Me_3SiCl/H_2SiCl_2 ratios should give long-chain $Me_3SiO[SiH_2O]_nSiMe_3$ species, but the formation of cyclic $[H_2SiO]_m$ products should become more important as well.

Of the three methods for the preparation of linear $[SiH_2O]_n$ polymers with unreactive end groups that we have studied, the equilibration of the $[H_2SiO]_m$ cyclic oligomers with hexamethyldisiloxane appears to be the most easily effected. With a useful route for the preparation of such polysiloxanes now available, the way is open for studies of their properties and for the development of possible applications.

Comments Concerning the Spectroscopic Properties of the Si–H Bond in Polysiloxanes. The present studies have provided a number of polysiloxanes containing Si–H bonds, thus permitting an investigation of the effect of the molecular environment on the Si–H stretching frequency in the IR spectrum and on the proton chemical shift in the NMR spectrum.

The Si–H stretching frequency in a $Me_3SiO[SiH_2O]_nSiMe_3$ system depends on the number of SiH_2O groups in the chain. ν(SiH): $Me_3SiOSiH_2OSiMe_3$, 2158 cm^{-1}; $Me_3SiO[SiH_2O]_2SiMe_3$, 2170 cm^{-1}; $Me_3SiO(SiH_2O)_3SiMe_3$, 2178 cm^{-1}.

The same is true for $HMe_2SiO[SiH_2O]_nSiMe_2H$ systems. ν(SiH): $HMe_2SiOSiH_2OSiMe_2H$, 2160 cm^{-1} (ν(SiH) of HMe_2Si, 2137 cm^{-1}); $HMe_2SiO[SiH_2O]_2SiMe_2H$, 2175 cm^{-1} (ν(SiH) of HMe_2Si, 2140 cm^{-1}); $HMe_2SiO[SiH_2O]_3SiMe_2H$, 2181 cm^{-1} (ν(SiH) of HMe_2Si, 2140 cm^{-1}).

The limiting value of 2190–2195 cm^{-1} is reached in systems with longer SiH_2O chains. ν(SiH): $MeSiH_2O[SiH_2O]_nSiH_2Me$ ($\bar{n}$ ~ 15), 2194 cm^{-1}; $Me_3SiO[SiH_2O]_nSiMe_3$ ($\bar{n}$ ~ 27), 2190 cm^{-1}; $Et_3SiO[SiH_2O]_nSiEt_3$ ($\bar{n}$ ~ 26), 2190 cm^{-1}; $ClSiH_2O[SiH_2O]_nSiH_2Cl$ ($\bar{n}$ ~ 24), 2195 cm^{-1}.

The Si–H stretching frequencies of $-OSiH_2O-$, HMe_2SiO-, and O_3SiH units are easily distinguished. ν(SiH): $[HMe_2SiO]_3SiH$, 2219 cm^{-1} (O_3SiH), 2137 cm^{-1} (HMe_2Si); $(HMe_2SiO)_2Si(H)OSiH_2OSiMe_2H$, 2172 cm^{-1} (SiH_2); 2140 cm^{-1} (HMe_2Si), 2220 cm^{-1} (O_3SiH); $[Me_3SiO]_3SiH$, 2205 cm^{-1}; $[Me_3SiO]_2Si(H)OSiH_2OSiMe_3$; 2171 cm^{-1} (SiH_2), 2205 cm^{-1} (O_3SiH). Thus, the Si–H stretching frequency provides good qualitative indication of the types of Si–H bonds that are present in the siloxane system.

The proton chemical shift of an SiH_2 unit in a polysiloxane also is dependent on its environment: $Me_3SiOSiH_2OSiMe_3$, δ_{SiH} 4.50; $Me_3SiO[SiH_2O]_2SiMe_3$, δ_{SiH} 4.57; $Me_3SiOSiH_2{}^aOSiH_2{}^bOSiH_2{}^aOSiMe_3$, δ_{SiH^a} 4.59, δ_{SiH^b} 4.64; $CH_3SiH_2O[SiH_2O]_nSiH_2CH_3$, δ_{SiH} 4.67, δ_{MeSiH_2} 4.63; $Et_3SiO[SiH_2O]_nSiEt_3$, δ_{SiH} 4.65; $ClSiH_2O[SiH_2O]_nSiH_2Cl$, δ_{SiH} 4.68, δ_{SiH_2Cl} 5.14.

Experimental Section

General Comments. Dichlorosilane was purchased in gas cylinders containing 10 lb of material from the Linde Division of the Union Carbide Corp. Since explosions could result if suck-back occurs, a regulator outlet equipped with a diffusion-resistant diaphragm seal valve and a check valve is essential in the setup for dispensing H_2-

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(7) Carmichael, J. B.; Heffel, J. *J. Phys. Chem.* **1965**, *69*, 2213.

(8) Eaborn, C. "Organosilicon Compounds"; Butterworths: London, 1961.

(9) On the basis of these observations, it seems likely that the earlier cohydrolysis experiments involving Me_3SiCl/H_2SiCl_2 mixtures[4,5] also took place with partial hydrolysis of Si–H bonds.

$SiCl_2$.[10] Note that it has been reported[11] that H_2SiCl_2/air mixtures can detonate violently.

IR spectra were recorded on a Perkin-Elmer 283B infrared spectrophotometer, proton NMR spectra with a Hitachi Perkin-Elmer R24B spectrometer, and ^{29}Si NMR spectra with a JEOL FX-90Q spectrometer operating at 17.76 MHz. A small amount of a relaxation agent, chromium(III) acetylacetonate, was added to all sample solutions in benzene-d_6. Some proton NMR spectra were recorded with a Bruker WM-270 instrument. $CDCl_3$ was the solvent used in all proton NMR measurements.

Preparation of Linear, Chlorine End-Blocked Polysiloxanes from Dichlorosilane. This experiment was carried out with a 300-mL three-necked, round-bottomed flask equipped with a magnetic stir bar, a pentane thermometer, a no-air septum, an addition funnel, and argon inlet tube, and a cold condenser. Diethyl ether (150 mL) was cannulated into the argon-filled flask that then was cooled in a dry ice/2-propanol bath to ca. −40 °C. Dichlorosilane was quantified (35.6 mL, 43.4 g, 0.43 mol) by condensing it into a graduated trap (at −40 °C), allowing the condensed liquid to warm nearly to room temperature, and then measuring the condensate volume (H_2SiCl_2 density is 1.22 g/cm^3 at 25 °C), before bubbling it as the vapor into the cold ether. Distilled water (7.20 g, 0.40 mL) was added dropwise over 7 min. The cold bath then was removed, and the clear, colorless reaction mixture was stirred at room temperature for 30 min. Subsequently the solvent and volatiles were removed by trap-to-trap distillation (room temperature (0.1 mmHg)) into a cold trap. A clear, colorless, slightly viscous oil remained behind (10.85 g, 53% yield). The 60-MHz ^1H NMR spectrum (in $CDCl_3$) showed singlets at δ 4.7 ($OSiH_2O$) and 5.15 (SiH_2Cl) in an integrated ratio of 15.5, which indicates the *average* constitution $ClSiH_2O[SiH_2O]_{31}SiH_2Cl$. This oil was rapidly converted to an insoluble, brittle solid on exposure to atmospheric moisture, and HCl was evolved.

GLC analysis of the trap-to-trap distillate showed the presence of $[H_2SiO]_4$ (25.5% by weight of GLC-detected products), $[H_2SiO]_5$ (66%), $[H_2SiO]_6$ (5.3%), $[H_2SiO]_7$ (1.6%), and $[H_2SiO]_8$ (0.8%). (Note characterization of these in ref 2.) The distillate was concentrated (atmospheric pressure, 40 °C maximum pot temperature) to leave 8.3 g of a clear liquid whose ^1H NMR spectrum showed only a singlet at δ 4.7. GLC analysis of this liquid showed the presence of the following cyclic $[H_2SiO]_m$ (*m*, weight percent of total $[H_2SiO]_n$ given): 4, 17; 5, 47; 6, 17.5; 7, 7.5; 8, 4.2; 9, 2.4; 10, 1.7; 11, 1.1; 12, 0.6; 13, 0.35; 14, 0.2; 15, trace.

In another such experiment, 42.0 g of H_2SiCl_2 in 150 mL of diethyl ether was treated with 6.83 g of water (same procedure) to give, after trap-to-trap distillation, 10.8 g (54%) of a clear, colorless oil. The proton NMR spectra showed the same singlets; their integrated ratio indicated the average composition $ClSiH_2O[SiH_2]_{23}SiH_2Cl$. Anal. Calcd for $Si_{25}H_{50}O_{24}Cl_2$: Si, 58.15; H, 4.17; Cl, 5.87. Found: Si, 57.03; H, 4.15; Cl, 5.27. IR (neat, KBr plates): 2195 (vs, ν(SiH)), 1100 (br, vs, ν_{as}(SiOSi)), 1000–830 with maximum at 850 (br, vs, $\delta(SiH_2)$ region), 720 (vs, γ(SiH)), 530 (m, SiCl?) cm^{-1}. ^{29}Si NMR (C_6D_6): δ −30.2 (t, $J(^{29}Si{-}^1H)$ = 277.6 Hz, $ClSiH_2$), −47.8 (t, $J(^{29}Si{-}^1H)$ = 260.7 Hz, $ClSiH_2O\mathit{Si}H_2$–), −49.0 (t, $J(^{29}Si{-}^1H)$ = 257.4 Hz, all other SiH_2O).

When the hydrolysis of dichlorosilane (0.43 mol) with 0.40 mol of water was carried out in pentane (150 mL) medium at ∼−40 °C by this procedure, the water crystallized as it was added. Upon removal of the cold bath, as the mixture warmed, the reaction commenced and a large amount of HCl was evolved, forming bubbles on the surface of the ice. The ice disappeared within 45 min, and a second liquid phase remained. The usual workup left 9.95 g (49%) of residue after trap-to-trap distillation. Integration of the δ 4.7 and 5.15 signals in the NMR spectrum established the average composition $ClSiH_2O[SiH_2O]_{27.6}SiH_2Cl$. The volatiles contained $[H_2SiO]_4$ (52.0%), $[H_2SiO]_5$ (35.6%), $[H_2SiO]_6$ (7.3%), and $[H_2SiO]_7$ (0.9%) (weight percent of total amount of GLC-detected siloxanes).

Reactions. $ClSiH_2O[SiH_2O]_nSiH_2Cl$ with Methylmagnesium Bromide. A 250-mL three-necked flask equipped with a magnetic stir bar, a low-temperature thermometer, an argon inlet tube, and an addition funnel was charged with 8.40 g of $ClSiH_2O[SiH_2O]_{23}SiH_2Cl$ (average composition), 30 mL of dry hexane, and 20 mL of dry Et_2O. The solution was cooled to −40 °C, and a solution of 0.04 mol of CH_3MgBr in Et_2O was added dropwise over 5 min. A white precipitate resulted. After 30 min following completion of the addition, 0.046 mol of Me_3SiCl was added to quench unconverted CH_3MgBr. The reaction mixture was warmed to room temperature and stirred for 1 h. Filtration (drybox) left a white solid that contained magnesium halide and a large amount of silicon-containing material. Removal of volatiles from the filtrate by trap-to-trap distillation (room temperature (0.1 mmHg)) left 3.7 g of a slightly viscous oil, $n^{20}D$ = 1.3951. The 60-MHz ^1H NMR spectrum ($CDCl_3$) showed a triplet at δ 0.34 (CH_3), a quartet ($J \sim 3$ Hz) at δ 4.63 ($CH_3Si\mathit{H}_2$), and a singlet at δ 4.67 ($OSiH_2O$) with $J(^{29}Si{-}^1H)$ = 255 Hz. Integration of the δ 4.67 and 0.34 signals gave the average composition $CH_3SiH_2O[SiH_2O]_{14}SiH_2CH_3$. Anal. Calcd for $C_2H_{38}O_{15}Si_{16}$: C, 3.20; H, 5.09; Si, 59.78. Found: C, 3.35; H, 5.08; Si, 59.95. IR (neat, KBr plates): 2964 (m, $\nu_{as}(CH_3)$), 2194 (vs, ν(SiH)), 1258 (m, Si–CH_3), 1095 (br, vs, ν_{as}(SiOSi)), 1000–830 with maximum at 850 (br, vs), 715 (vs, γ(SiH)). ^{29}Si NMR (C_6D_6): δ_{Si} −19.4 (t, $J(^{29}Si{-}^1H)$ = 219 Hz, CH_3SiH_2), −48.2 (t, $J(^{29}Si{-}^1H)$ = 254.1 Hz, $CH_3SiH_2OSiH_2$), −49.0 (t, $J(^{29}Si{-}^1H)$ = 257.4 Hz, all other SiH_2).

When such a reaction was carried out at room temperature (using 8.5 g of the $ClSiH_2O[SiH_2O]_nSiH_2Cl$ obtained by hydrolysis of 0.432 mol of H_2SiCl_2 with 0.41 mol of H_2O in 150 mL of Et_2O at −40 °C), otherwise with the same procedure, in the addition of 0.027 mol of CH_3MgBr and 0.046 mol of Me_3SiCl, 6.0 g of a clear, slightly viscous oil, $n^{20}D$ = 1.3973, was obtained. The ^1H NMR spectrum was identical with the one of the product of the −50 °C reaction above except for the presence of doublet at δ 0.24 ($J \sim 3$ Hz), indicative of some –OSi(H)(CH_3)O– units in the chain. Integration of the appropriate signals in the NMR spectrum established the average composition $CH_3SiH_2O[SiH_2O]_{30.33}[Si(H)(CH_3)O]_{1.33}SiH_2CH_3$. The ^{29}Si NMR spectrum (C_6D_6) of this product showed the presence of the –OSi(H)(CH_3)O– unit: an additional signal at δ_{Si} −2.0 was observed. Anal. Calcd for $C_{3.33}H_{76.64}O_{33}Si_{34}$: C, 2.50; H, 4.83; Si, 59.68. Found: C, 2.30; H, 4.82; Si, 58.68.

$ClSiH_2O[SiH_2O]_nSiH_2Cl$ with Trialkylsilanols. (a) Trimethylsilanol. A 10-mL three-necked flask equipped with a magnetic stir bar, a no-air rubber septum, a thermometer, and an argon inlet tube was charged with 1.4762 g of $ClSiH_2O[SiH_2O]_{31}SiH_2Cl$ and 4 mL of dry Et_2O. Trimethylsilanol (0.491 g, 5.45 mmol, prepared[12] by W.–L. Wang) was then added all at once. A second liquid phase separated, and a small amount of gas was evolved. The reaction mixture was stirred at room temperature for 15 min and then was trap-to-trap distilled (room temperature (0.1 mmHg)) to remove volatiles. A clear, slightly viscous liquid (1.6473 g; $n^{20}D$ = 1.3957) remained behind. Its proton NMR spectrum ($CDCl_3$) showed a singlet at δ 0.16 (Me_3Si), a small resonance at δ 4.36 (O_3SiH), a singlet at δ 4.55 ($Me_3SiOSi\mathit{H}_2$), and a singlet at δ 4.62 (all other SiH_2). Integration of the appropriate signals established the composition $Me_3SiO[SiH_2O]_{27}(Si(H)(OSiMe_3))_{2.0}SiMe_3$. The ^{29}Si NMR spectrum (C_6D_6) showed the Me_3Si signal at δ_{Si} +12.7, SiH_2 resonances at δ_{Si} −49.0, −49.6, −50.3, and −51.0, and the O_3SiH resonance at δ_{Si} −82.3. Anal. Calcd for $C_{12}H_{92}O_{32}Si_{33}$: C, 8.60; H, 5.53; Si, 55.31. Found: C, 8.64; H, 5.55; Si, 55.44.

A similar reaction, carried out initially at −50 °C, with subsequent warming to room temperature, gave, after removal of volatiles, a slightly viscous oil, $n^{20}D$ = 1.3975, in 94% yield. The ^1H NMR spectrum of this product showed no signal at δ 4.36 due to –OSi(H)($OSiMe_3O$)– units.

(b) Triethylsilanol. Triethylsilanol (1.76 g, 0.12 mol, Petrarch) was added by syringe to a solution of 7.6 g of $ClSiH_2O[SiH_2O]_{31}SiH_2Cl$ in 20 mL of dry Et_2O under argon. The resulting solution was stirred at room temperature for 30 min and then was trap-to-trap distilled (room temperature (0.1 mmHg)). The residue was a colorless oil (8.4 g; $n^{20}D$ = 1.4086). The ^1H NMR spectrum ($CDCl_3$) showed a multiplet at δ 0.5–1.2 due to the Et_3Si group, a singlet at δ 4.65 due to SiH_2, and a very small signal at δ 4.36 due to O_3SiH. Integration of the appropriate signals estalished the average composition $Et_3SiO[SiH_2O]_{26.4}[Si(H)(OSiEt_3)]_{0.22}SiEt_3$. The ^{29}Si NMR spectrum (C_6D_6) showed the Et_3Si signal at δ_{Si} +15.0, SiH_2 resonances at δ_{Si}

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(10) Materials Safety Data Sheet, Union Carbide Silane A-199 (Linde Division, Union Carbide Corp.); Linde Specialty Gases Safety Precautions and Emergency Procedures, F-12-237.

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Table III. Equilibration of $[H_2SiO]_m$ with $Me_3SiOSiMe_3$ ($SiH_2O/Me_3SiOSiMe_3$ Molar Ratio 1.79)[a]

"n" in $Me_3SiO[SiH_2O]_nSiMe_3$	amt, mmol	mol % of total $Me_3SiO[SiH_3O]_nSiMe_3$
0	4.18	19.0
1	7.18	32.6
2	5.65	25.7
3	2.97	13.5
4	1.21	5.50
5	0.43	1.95
6	0.13	0.59
7	0.033	0.15

[a] Reaction of 20.4 mmol of $Me_3SiOSiMe_3$, 36.5 mmol of SiH_2O, 0.0418 g of concentrated H_2SO_4, and 0.395 g of CH_2Cl_2 for 5 h at 70 °C.

Table IV. Equilibration of $[H_2SiO]_m$ with $Me_3SiOSiMe_3$ ($SiH_2O/Me_3SiOSiMe_3$ Molar Ratio 0.90)[a]

"n" in $Me_3SiO[SiH_2O]_nSiMe_3$	amt, mmol	mol % of total $Me_3SiO[SiH_2O]_nSiMe_3$
0	4.30	36.8
1	4.67	40.0
2	2.01	17.2
3	0.58	4.97
4	0.10	0.85
5	0.015	0.13

[a] Reaction of 10.7 mmol of $Me_3SiOSiMe_3$, 9.6 mmol of SiH_2O, 0.0512 g of concentrated H_2SO_4, and 0.103 g of CH_2Cl_2 for 3 h at 70 °C.

Table V. Equilibration of $[H_2SiO]_m$ with $Me_3SiOSiMe_3$ ($SiH_2O/Me_3SiOSiMe_3$ Molar Ratio 0.60)[a]

"n" in $Me_3SiO[SiH_2O]_nSiMe_3$	amt, mmol	mol % of total $Me_3SiO[SiH_2O]_nSiMe_3$
0	7.91	52.5
1	5.38	35.7
2	1.55	10.3
3	0.20	1.32
4	0.037	0.25

[a] Reaction of 14.1 mmol of $Me_3SiOSiMe_3$, 8.6 mmol of SiH_2O, 0.046 g of concentrated H_2SO_4, and 0.093 g of CH_2Cl_2 for 3 h at 70 °C.

−49.0, −49.8, −50.3, and −50.9, and the O_3SiH signal at δ_{Si} −82.4. Anal. Calcd for $C_{13.3}H_{86.3}O_{27.8}Si_{28.8}$: C, 10.64; H, 5.80; Si, 53.91. Found: C, 10.67; H, 5.74; Si, 53.01.

Sulfuric Acid Catalyzed Equilibration of Cyclic $[H_2SiO]_m$ Oligomers with Hexamethyldisiloxane. A mixture of cyclic $[H_2SiO]_m$ oligomers was prepared as follows. a 1-L three-necked round-bottomed flask equipped with a magnetic stir bar, an argon inlet tube, a no-air rubber septum, a low-temperature thermometer, and a cold condenser was filled with argon, and 500 mL of dichloromethane was added. The flask was cooled to ∼−40 °C, and then 68.4 g (0.641 mol) of H_2SiCl_2 (quantified as described above) was bubbled into the dichloromethane. Distilled water (11.0 g, 0.615 mol) was added by syringe over 20 min. Ice formed in the mixture. Subsequently, the temperature was allowed to rise slowly to −10 °C. The hydrolysis reaction became rapid at ∼−15 °C as evidenced by HCl evolution and ice consumption. The colorless solution that was obtained on warming to room temperature was washed with five 350-mL portions of cold water. The organic layer was separated and dried over $MgSO_4$ while being kept at −8 °C. Filtration was followed by distillation at atmospheric pressure until a pot temperature of 75 °C. A clear liquid (28.2 g) remained behind. A 26.6-g portion of this liquid was trap-to-trap distilled (heat gun (0.05 mmHg)) into a receiver at −196 °C. The residue (10.3 g) was a slightly viscous oil. The distillate (16.3 g) was examined by GLC and by ^1H NMR. It contained 19% by weight of CH_2Cl_2 and 81% $[H_2SiO]_m$. The composition of the latter (m, wt%) was as follows: 4, 12.2; 5, 51.8; 6, 24.1; 7, 5.3; 8, 2.45; 9, 1.8; 10, 1.2; 11, 0.66; 12, 0.29; 13, 0.05. This mixture was used in the equilibration reaction.

Predetermined amounts of the $[H_2SiO]_m$ and hexamethyldisiloxane and sulfuric acid (Mallinckrodt-ACS, 95.4%) (about 1 wt%) were charged into a 10-mL round-bottomed flask equipped with an argon inlet, a magnetic stir bar, a water-cooled condenser, and a no-air rubber septum. The reaction mixtures were stirred and heated under argon at 70 °C for about 3 h. After cooling to room temperature, they were washed with dilute sodium bicarbonate and then with water and dried.

The equilibrated mixtures were analyzed by GLC (Hewlett-Packard Model 5750 linear temperature-programmed gas chromatograph, 6 ft × $^1/_4$ in. column packed with 20% SE-30 silicone rubber gum on 80–100 mesh Chromosorb P (acid washed and treated with Me_2SiCl_2); 30–250 °C temperature program at 10 °C/min; toluene internal standard). Empirical weight response factors for $Me_3SiOSiMe_3$, $Me_3SiOSiH_2OSiMe_3$, and $Me_3SiO(SiH_2O)_2SiMe_3$ were determined. For higher $Me_3SiO[SiH_2O]_nSiMe_3$ the response factors were estimated by extrapolation. The results of the experiments that were carried out are given in Tables II–V.

At room temperature, such equilibrations were very much slower.

Cohydrolysis of Dichlorosilane and Trimethylchlorosilane and Dimethylchlorosilane. (a) Addition of the Aqueous System to the Chlorosilanes. As an example, a cohydrolysis of Me_2HSiCl with H_2SiCl_2 is described.

A 200-mL three-necked flask equipped with a gas inlet tube, a cold condenser, an addition funnel, and a magnetic stir bar was evacuated and filled with nitrogen and then was charged with 23.82 g (0.252 mol) of Me_2HSiCl and 60 mL of diethyl ether. The solution was cooled to 0–5 °C, and then, with the procedure described above, 12.7 g (0.126 mol) of H_2SiCl_2 was allowed to evaporate into the solution. Subsequently, 5.0 mL of distilled water was added, dropwise over 10 min, while the temperature in the flask was maintained at 0–10 °C. Then, another 50 mL of water was added more rapidly, and the resulting mixture was stirred for 3 h at room temperature. The ether layer then was separated and washed with distilled water until the washings were neutral. Drying over anhydrous $MgSO_4$ was followed by removal of the solvent by careful distillation under nitrogen at atmospheric pressure. The composition of the residue was examined by GLC, and samples of the lower boiling products were collected by GLC for spectroscopic and analytical characterization.

When an excess of water was added to a 1:2 mixture of H_2SiCl_2 and Me_3SiCl in diethyl ether by this procedure, the following products were isolated by GLC: $Me_3SiOSiMe_3$ (24% by weight of major producst), $Me_3SiOSiH_2OSiMe_3$ (25), $Me_3SiO[SiH_2O]_2SiMe_3$ (7.5), $Me_3SiO[SiH_2O]_3SiMe_3$ (<1), $[Me_3SiO]_3SiH$ (12), $[Me_3SiO]_2Si(H)OSiH_2OSiMe_3$ (14).

A similar addition of water to an ether solution of H_2SiCl_2 and Me_2HSiCl in 1:2 molar ratio gave the following results: $Me_2HSiOSiMe_2H$ (31), $HMe_2SiOSiH_2OSiMe_2H$ (3.3), $HMe_2SiO[SiH_2O]_2SiMe_2H$ (1.7), $HMe_2SiO[SiH_2O]_3SiMe_2H$ (<1), $[HMe_2SiO]_3SiH$ (29), $[HMe_2SiO]_2Si(H)OSiH_2OSiMe_2H$ (12).

Addition instead of a 1:1 NaH_2PO_4/NaH_2PO_4 buffer solution to an ether solution of H_2SiCl_2 and Me_2HSiCl in 1:2 molar ratio gave the following results: $Me_2HSiOSiMe_2H$ (37), $HMe_2SiOSiH_2OSiMe_2H$ (31), $HMe_2SiO[SiH_2O]_2SiMe_2H$ (13), $HMe_2SiO[SiH_2O]_3SiMe_2H$ (3.7), $[HMe_2SiO]_3SiH$ (3.7), $[HMe_2SiO]_2Si(H)OSiH_2OSiMe_2H$ (5.6).

(b) Addition of the Chlorosilanes to an Aqueous 1:1 NaH_2PO_4/Na_2HPO_4 Buffer Solution. As an example, a cohydrolysis of Me_2HSiCl and H_2SiCl_2 is described.

A 2-L three-necked round-bottomed flask equipped with a nitrogen inlet tube, a cold condenser, a mechanical stirrer, and a no-air rubber septum was evacuated and filled with nitrogen. It then was charged with 138 g (1 mol) of $NaH_2PO_4 \cdot H_2O$ and 142 g (1 mol) of Na_2HPO_4 and 1200 mL of distilled water. The resulting solution was cooled to 0–5 °C. A 200-mL three-necked flask equipped with a gas inlet tube, a cold condenser, and a magnetic stir bar was evacuated and filled with nitrogen and then was charged with 45.93 g (0.486 mol) of Me_2HSiCl and 109 mL of diethyl ether. This solution was cooled to 0–5 °C, and the 24.5 g (0.243 mol) of H_2SiCl_2 was added by the procedure described above.

The Me_2HSiCl/H_2SiCl_2 solution then was added via cannula with nitrogen pressure to the aqueous buffer solution over 10 min. The organic layer was separated, washed with distilled water, dried over $MgSO_4$ and distilled to remove solvent. The residual liquid was examined by GLC. Pure samples of the lower boiling products for spectroscopic and analytical characterization were isolated by GLC.

This experiment gave the following products in the indicated weight percent of the major products: $(Me_2HSi)_2O$ (54), $HMe_2SiOSiH_2OSiMe_2H$ (18), $HMe_2SiO[SiH_2O]_2SiMe_2H$ (13),

$HMe_2SiO[SiH_2O]_3SiMe_2H$ (8.0). $[HMe_2SiO]_3SiH$ and $[HMe_2SiO]_2Si(H)OSiH_2OSiMe_2H$ were not present.

Addition of a 1:2 mixture of H_2SiCl_2 and Me_3SiCl in Et_2O to the buffer solution at 0–10 °C gave the following products: $Me_3SiOSiMe_3$ (44), $Me_3SiOSiH_2OSiMe_3$ (28), $Me_3SiO[SiH_2O]_2SiMe_3$ (18), $Me_3SiO[SiH_2O]_3SiMe_3$ (7.5). Here also, products of Si–H hydrolysis were not present.

More such Me_3SiCl/H_2SiCl_2 cohydrolysis experiments are summarized in Table I. The following siloxanes were isolated and characterized.

$Me_3SiOSiH_2OSiMe_3$: $n^{20}_{\mathrm{D}} = 1.3809$. Anal. Calcd for $C_6H_{20}O_2Si_3$: C, 34.57; H, 9.67. Found: C, 34.51; H, 9.69. ^1H NMR ($CDCl_3$): δ 0.14 (s, 18 H, Me_3Si), 4.50 (s, 2 H, SiH_2, $J(^{29}Si-^1H) = 243$ Hz).

$Me_3SiO[SiH_2O]_2SiMe_3$: $n^{20}_{\mathrm{D}} = 1.3828$. Anal. Calcd for $C_6H_{22}O_3Si_4$: C, 28.31; H, 8.71. Found: C, 28.38; H, 8.67. ^1H NMR ($CDCl_3$): δ 0.15 (s, 18 H, Me_3Si), 4.57 (s, 4 H, SiH_2, $J(^{29}Si-^1H) = 248$ Hz).

$Me_3SiO[SiH_2O]_3SiMe_3$: $n^{20}_{\mathrm{D}} = 1.3847$. Anal. Calcd for $C_6H_{24}O_4Si_5$: C, 23.97; H, 8.05. Found: C, 24.24; H, 8.13. ^1H NMR ($CDCl_3$): δ 0.15 (s, 18 H, Me_3Si), 4.59 (s, 4 H, $Me_3SiOSiH_2$, $J(^{29}Si-^1H) = 252$ Hz), 4.64 (s, 2 H, center SiH_2, $J(^{29}Si-^1H) = 252$ Hz).

$[Me_3SiO]_3SiH$: $n^{20}_{\mathrm{D}} = 1.3861$. Anal. Calcd for $C_9H_{28}O_3Si_4$: C, 36.44; H, 9.51. Found: C, 36.18; H, 9.57. ^1H NMR ($CDCl_3$): δ 0.12 (s, 27 H, Me_3Si), 4.20 (s, 1 H, SiH).

$[Me_3SiO]_2Si(H)OSiH_2OSiMe_3$: $n^{20}_{\mathrm{D}} = 1.3882$. Anal. Calcd for $C_9H_{30}O_4Si_5$: C, 31.54; H, 8.82. Found: C, 31.69; H, 8.93. ^1H NMR ($CDCl_3$): δ (0.15 (s, 27 H, Me_3Si), 4.20 (s, 1 H, O_3SiH), 4.54 (s, 2 H, SiH_2).

$HMe_2SiOSiH_2OSiMe_2H$: $n^{20}_{\mathrm{D}} = 1.3756$. Anal. Calcd for $C_4H_{16}O_2Si_3$: C, 26.63; H, 8.94. Found: C, 26.85; H, 8.82. ^1H NMR ($CDCl_3$): δ 0.23 (d, 12 H, Me_2Si), 4.53 (s, 2 H, SiH_2, $J(^{29}Si-^1H) = 248$ Hz), 4.68 (hept, 2 H, Me_2SiH).

$HMe_2SiO[SiH_2O]_2SiMe_2H$: $n^{20}_{\mathrm{D}} = 1.3798$. Anal. Calcd for $C_4H_{18}O_3Si_4$: C, 21.21; H, 8.01. Found: C, 21.12; H, 7.95. ^1H NMR ($CDCl_3$): δ 0.23 (d, 12 H, Me_2Si), 4.58 (s, 4 H, SiH_2, $J(^{29}Si-^1H) = 250$ Hz), 4.69 (hept, 2 H, Me_2SiH).

$HMe_2SiO[SiH_2O]_3SiMe_2H$: $n^{20}_{\mathrm{D}} = 1.3823$. Anal. Calcd for $C_4H_{20}O_4Si_5$: C, 17.62; H, 7.39. Found: C, 17.60; H, 7.33.

$[HMe_2SiO]_3SiH$: $n^{20}_{\mathrm{D}} = 1.3822$. Anal. Calcd for $C_6H_{22}O_3Si_4$: C, 28.31; H, 8.71. Found: C, 28.22; H, 8.65. ^1H NMR ($CDCl_3$): δ 0.22 (d, 18 H, Me_2Si), 4.20 (s, 1 H, O_3SiH), 4.69 (hept, 3 H, Me_2SiH).

$[HMe_2SiO]_2Si(H)OSiH_2OSiMe_2H$: $n^{20}_{\mathrm{D}} = 1.3845$. Anal. Calcd for $C_6H_{24}O_4Si_5$: C, 23.97, H, 8.05. Found: C, 23.95; H, 8.02. ^1H NMR ($CDCl_3$): δ 0.23 (d, 18 H, Me_2Si), 4.25 (s, 1 H, O_3SiH), 4.58 (s, 2 H, SiH_2), 4.70 (hept, 3 H, Me_2SiH).

Acknowledgment. The authors are grateful to the U.S. Air Force Office of Scientific Research, (NC)–AFSC, and to the Rhône-Poulenc Co. for support of this research. D.S. acknowledges, with thanks, an Alexander von Humboldt Prize, awarded by the Alexander von Humboldt Foundation, Bad Godesberg, during the tenure of which this paper was written.

Registry No. SiH_2Cl_2, 4109-96-0; CH_3Br, 74-83-9; Me_3SiOH, 1066-40-6; Et_3SiOH, 597-52-4; $Me_3SiOSiMe_3$, 107-46-0; Me_3SiCl, 75-77-4; Me_2SiHCl, 1066-35-9; $Me_3SiOSiH_2OSiMe_3$, 93254-88-7; $Me_3SiO[SiH_2O]_2SiMe_3$, 93254-89-8; $Me_3SiO[SiH_2O]_3SiMe_3$, 93254-90-1; $[Me_3SiO]_3SiH$, 1873-89-8; $[Me_3SiO]_2Si(H)OSiH_2OSiMe_3$, 93254-91-2; $HMe_2SiOSiH_2OSiMe_2H$, 20363-25-1; $HMe_2SiO[SiH_2O]_2SiMe_2H$, 93254-92-3; $[HMe_2SiO]_3SiH$, 17449-78-4; $[HMe_2SiO]Si(H)OSiH_2OSiMe_2H$, 93254-93-4; $HMe_2SiO[SiH_2O]_3SiMe_2H$, 93254-94-5.

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An Electroactive Polymer Film on a Mercury Electrode Based on a Thallium Macrocyclic Polyether Complex

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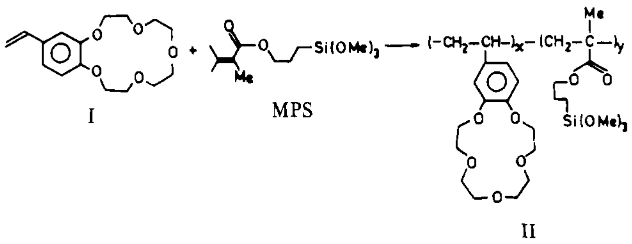
Received February 23, 1984

Films of a copolymer of 4-vinylbenzo-15-crown-5 and (3-methacryloxypropyl)trimethoxysilane were formed and cross-linked on mercury electrodes by solution evaporation followed by exposure to moist HCl vapor. The films in-partition ions complexed by the polyether crown, such as thallium(I) from acetonitrile solution. After partitioning and transfer of the coated electrode to a thallium-free solution, electrochemical waves due to reduction of crown-complexed thallium to mercury amalgam, and the reverse, can be observed. In the presence of thallium in the solution, both crown-complexed and free thallium waves appear. Many monomolecular layer equivalents of crown-complexed thallium react in a cyclic voltammogram, and it is proposed that the thallium migrates to the electrode by hopping between crown sites.

Macrocyclic polyethers (crown ethers) have been the focus of much research since recognition of their properties as selective complexing agents.[1] They are typically uncharged compounds with an internal oxygen-donor-rich cavity capable of cation encapsulation, with selectivity toward cations being primarily a function of the number of oxygen donors and ring size. Applications of crown ethers have been quite diverse, including phase-transfer catalysis, stabilization of Na^- ions, and utilization in ion-selective membrane electrodes.[2]

Scheme I



An important goal in the chemical design of electrode surfaces is the transposition of known chemistry of dissolved substances to the electrode surface. This has been of interest to us and others[3] in the design of monolayer films and polymeric multilayer films on electrodes. Recent work has included polyionic ion-exchanging polymer films[4] on electrodes, capable

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