[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polyalkylene Disulfides and Polysulfides Containing Silicon[1]

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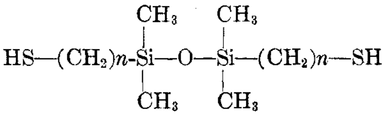
The catalytic air oxidation of 1,3-di(2-mercaptoethyl)tetramethyldisiloxane and 1,3-di(3-mercaptopropyl)tetramethyldisiloxane to form high molecular weight polydisulfides has been carried out in a soap emulsion system. Higher temperatures of oxidation were found to result in significantly higher molecular weights for the polymers. Treatment of these polydisulfides with sulfur resulted in the formation of rubbery polypolysulfides. Some oxidations were carried out using mixtures of 1,3-di(3-mercaptopropyl)tetramethyldisiloxane and 1,4-dimercaptobutene-2 (a new compound), but the soluble polymers isolated appeared by analysis and infrared spectrum to be exclusively homopolymers of the dimercaptodisiloxane monomer.

In the search for useful elastomeric materials possessing good low temperature properties and good solvent resistance, the investigation of the class of polymeric disulfides containing disiloxane linkages was a logical choice.[3,4] As previous work in this laboratory had shown the efficacy of catalytic air oxidation of α,ω-alkylene dimercaptans in an emulsion system for the formation of high molecular weight polymeric disulfides,[5] appropriate α,ω-alkylene dimercaptans containing disiloxane linkages were synthesized. The dimercaptans used in this investigation were 1,3-di-(2-mercaptoethyl)-tetramethyldisiloxane (I) and 1,3-di-(3-mercaptopropyl)-tetramethyldisiloxane (II). Both monomers were obtained by the addition of thiolacetic acid to the corresponding diolefinic disiloxanes, followed by saponification of the resultant dithioacetates. Monomer II was synthesized by the procedure of Marvel and Cripps.[6] It was found in the synthesis of monomer I, by the addition of thiolacetic acid to 1,3-divinyltetramethyldisiloxane, that the use of twice freshly distilled thiolacetic acid was required to avoid the formation of the monoaddition product even though excess thiolacetic acid was used. No such difficulty was experienced in the addition of thiolacetic acid to 1,3-diallyltetramethyldisiloxane to form the dithioacetate of monomer II.



$$HS-(CH_2)_n-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-(CH_2)_n-SH$$

I. $n = 2$
II. $n = 3$

Catalytic air oxidations were carried out using a standardized emulsion recipe developed by Marvel and Olson.[5] The effect of the temperature at which the oxidation of the dimercaptan was carried out on the molecular weight of the resultant polymeric disulfides was investigated. It was found that higher temperatures favored higher molecular weights with the exception that above 80° the product of the oxidation of I tended to undergo secondary reactions with the formation of crosslinked insoluble polymer (see Table I).

TABLE I

CATALYTIC AIR OXIDATION[a] OF 1,3-DI(2-MERCAPTOETHYL)-TETRAMETHYLDISILOXANE (I)

Temp.	Yield[b] %	Inherent Viscosity[c]	Remarks
Room	70	0.37	Mobile, tacky liquid
42	74	0.46	Viscous, tacky liquid
56	55	0.69	Tacky, semisolid[e]
80	62	0.77	Rubbery, semisolid[f]
89	85[d]	—	Crumbly, factice-like solid

[a] In an emulsion system, the recipe of which is given in the experimental section. [b] Yield after one reprecipitation from chloroform by methanol. [c] Viscosity of ~0.5% solution in chloroform. [d] Crude yield, insoluble in the usual solvents, *i.e.*, chloroform, benzene, dioxane-chloroform mixtures. [e] *Anal.* Calcd. for $(C_8H_{20}OS_2Si_2)_x$: S, 25.39; Si, 21.74. Found: S, 23.77; Si, 21.76. [f] *Anal.* Calcd. for $(C_8H_{20}OS_2Si_2)_x$: C, 38.05; H, 7.98; S, 25.39. Found: C, 38.23; H, 7.73; S, 21.87.

TABLE II

CATALYTIC AIR OXIDATION[a] OF 1,3-DI(3-MERCAPTOPROPYL)TETRAMETHYLDISILOXANE (II)

Temp.	Yield[b] %	Inherent Viscosity[c]	Remarks
Room	72	0.33	Mobile, tacky wax
56	78	0.56	Cohesive, tacky liquid[d]
80	82	0.67	Rubbery, viscous liquid
89	75	0.78	Rubbery semisolid[e]

[a] In an emulsion system for seven days, the recipe of which is given in the experimental section. [b] After one reprecipitation from chloroform by methanol. [c] Viscosity of ~0.5% solution in chloroform. [d] *Anal.* Calcd. for $(C_{10}H_{24}OS_2Si_2)_x$: S, 22.86; Si, 20.02. Found: S, 22.65; Si 20.09. [e] *Anal.* Found: S, 23.54; Si, 19.95

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[2] Visiting Scientist from the Indian Institute of Technology, Kharagpur, India, under the sponsorship of the U. S. State Department International Cooperation program and in part supported by NSF grant G-2626.

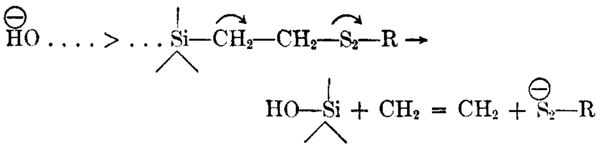
[3] For an example of the known solvent resistance of polydisulfide elastomers, see J. J. Prendergast, *Rubber Age*, **84**, No. 4, January 1959.

[4] For an example of the good low temperature properties and very low second order transition temperatures of silicone elastomers, see C. E. Weir, W. H. Leser and L. A. Wood, *J. Research, Natl. Bur. Standards*, **44**, 367 (1950).

[5] C. S. Marvel and L. E. Olson, *J. Am. Chem. Soc.*, **79**, 3089 (1957).

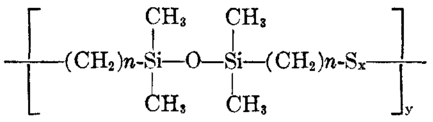
[6] C. S. Marvel and H. N. Cripps, *J. Polymer Sci.*, **9**, 53 (1952).

A possible explanation for the tendency of the polydisulfide of monomer I to undergo secondary reactions and of its consistently low analytical values for sulfur lies in the presence of a *beta*-substituted ethyl group attached to silicon atoms in the polymer chain. As this substituent, the disulfide group can be stabilized as an anion, cleavage by hydroxide ion (in the alkaline emulsion system), especially at higher temperatures, will be facilitated[7] yielding silanols capable of further condensations.



$$HO^{\ominus}\ldots\ldots>\ldots Si-CH_2-CH_2-S_2-R \rightarrow HO-Si + CH_2 = CH_2 + {}^{\ominus}S_2-R$$

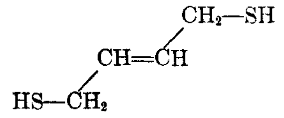
All of these polymeric disulfides (IIIa, IIIb) were essentially liquids which exhibited cold flow to a greater or less degree depending on their inherent viscosities. These polymeric disulfides could be treated with two gram atom equivalents of sulfur per base mole of disulfide links at 150° to form polysulfides,[8] IVa and IVb. These polypolysulfides were tough, rubbery, cohesive, non-tacky solids which no longer exhibited cold flow. Preliminary evaluations indicate them to be definitely elastomeric with good low temperature properties, but their solvent resistance was not satisfactory.[9] They are much more difficultly soluble in the usual organic solvents for the polydisulfides, III, *i.e.*, chloroform and benzene, but will dissolve eventually in a mixture of chloroform and dioxane, indicating the lack of any appreciable crosslinkages. It is interesting that the polypolysulfide IVb with $x = 2.7$ and $y = 5.2$ has been prepared in an alternate manner by Nasiak and Post[10] who added hydrogen polysulfide to allyldimethylethoxysilane in bulk and heated the resultant adduct to complete the condensation. Their polymer was reported to have a molecular weight of 1505 (by cryoscopic measurement in benzene) and an inherent viscosity of 0.15 (0.4% in chloroform).



$$\left[-(CH_2)_n-\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{CH_3}{\underset{CH_3}{Si}}-(CH_2)_n-S_x-\right]_y$$

IIIa. $n = 2, x = 2$
b. $n = 3, x = 2$
IVa. $n = 2, x = 3.5\text{–}3.7$
b. $n = 3, x = 3.5\text{–}3.7$

As these polydisulfides and polypolysulfides are essentially linear and soluble, an attempt was made to introduce reactive sites along the polymer chain which could serve for eventual crosslinking to increase the solvent resistance and perhaps the elastomeric nature of these polymers. For this purpose 1,4-dimercaptobutene-2 (V) was synthesized. It was obtained by the saponification of the di-isothiuronium salt formed from 1,4-dibromobutene-2. The *trans* structure is assigned on the basis of strong absorption in the infrared spectrum of 962 cm.$^{-1}$ (C–H out-of-plane deformation for *trans* disubstituted ethylenic double bond)[11a] and the absence of absorption in the region 1620–1680 cm.$^{-1}$.[11b]



V

In an attempt to prepare copolymers, mixtures of 2.5, 5.0, and 10% of V with monomer II were subjected to air oxidation in the emulsion system for seven days at 89°. The polymers which were isolated consisted of a chloroform soluble fraction and a completely insoluble fraction (chloroform, benzene, chloroform-dioxane, dimethylsulfoxide, dimethylsulfoxide-chloroform) (see Table III).

The infrared spectra of samples 1, 2 and 3, as well as the analytical data, indicates that the soluble polymers isolated were exclusively the homopolymer IIIb formed by oxidation of monomer II. It is difficult to explain the complete exclusion of monomer V from incorporation into a soluble copolymer with II. Premature crosslinking by addition of a terminal mercaptan group of a polymer chain across the internal double bond of a polymer chain containing an unsaturated dimercaptan unit would seem to be ruled out by the observations of Marvel and Cripps.[12]

EXPERIMENTAL

1,3-Di(2-thioacetoxyethyl)tetramethyldisiloxane. In a 500-ml. three necked flask equipped with stirring and reflux condenser was placed a solution of 76 g. (1.0 mol.) of thiolacetic acid (Matheson, Coleman and Bell, reagent grade, twice freshly distilled) in 250 ml. of cyclohexane (distilled from calcium hydride). A small amount of benzoyl peroxide was added and 1,3-divinyltetramethyldisiloxane (56 g., 0.30 mol.)[13] prepared by the acid hydrolysis of vinyldimethylethoxysilane (Penninsular ChemResearch, Inc.) in 75% yield, b.p. 136–137°, n_D^{25} 1.4103, was added quite rapidly. The temperature of the reaction rose quickly to

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[7] See, for example, P. D. George, M. Prober, and J. R. Eliot, *Chem. Revs.*, **56,** 1118 (1956). β-Chloroethylsilanes are quantitatively cleaved by base at room temperature with the elimination of ethylene and chloride ion.

[8] J. C. Patrick and S. M. Martin, *Ind. Eng. Chem.*, **28,** 1148 (1936).

[9] Private communication, Dr. Juan C. Montermoso, QC

[10] L. D. Nasiak and H. K. Post, *J. Org. Chem.*, **24,** 492 (1959).

[11] a. "The Infrared Spectra of Complex Molecules," L. J. Bellamy, John Wiley & Sons, Inc., New York (1956), p. 40. b. "The Infrared Spectra of Complex Molecules," L. J. Bellamy, John Wiley & Sons, Inc., New York (1956), p. 34, " . . . . no C=C stretching vibration will appear in the infrared from compounds with a *trans* double bond at the center of symmetry."

[12] C. S. Marvel and H. N. Cripps, *J. Polymer Sci.*, **8,** 313 (1952).

[13] W. Kantor, C. Osthoff, and D. T. Hurd, *J. Am. Chem. Soc.*, **77,** 1685 (1955).

TABLE III

Co-oxidation[a] of 1,4-Dimercaptobutene-2 (V) and 1,3-Di(3-mercaptopropyl)tetramethyldisiloxane (II)

Sample Run	II ml.	V ml.	Chloroform Soluble[b] %	η^c	Analyses[d] Found Si	S	Insoluble %
1	10.0	0.25	82	0.73	20.14	23.23	12
2	10.0	0.50	74	0.95	20.09	22.65	16
3	10.0	1.00	52	0.60	20.23	22.77	33

[a] In an emulsion system for seven days at 89°. [b] After one reprecipitation from chloroform into methanol. [c] Inherent viscosity (~0.5% in chloroform). [d] ANAL. Calcd. for $(C_{10}H_{24}OS_2Si_2)_n$ (IIIb): S, 22.86; Si, 20.02 for $(C_4H_6S_2)_n$ (Polymer from V). S, 54.25. If complete statistical incorporation of V into the polymer had taken place, for sample 3: S, 28.7; Si, 16.2.

about 65°. Reflux was applied for 8 hr. and then solvent and excess thiolacetic acid were removed by heating on a steam bath. Distillation of the residue gave 95 g. of product (93.3% yield) boiling at 146–150°/1.5 mm. Redistillation gave pure 1,3-di-(2-thioacetoxyethyl)-tetramethyldisiloxane, 85 g. (83% yield), b.p. 149–150°/1.6 mm., n_{D}^{25} 1.4839.

Anal. Calcd. for $C_{12}H_{26}O_3S_2Si_2$: C, 42.56; H, 7.74; S, 18.94; Si, 16.59. Found: C, 42.82; H, 7.40; S, 18.93; Si, 16.59.

1,3-Di-(2-mercaptoethyl)-tetramethyldisiloxane (I). To a solution of 85 g. of 1,3-di-(2-thioacetoxyethyl)-tetramethyldisiloxane (0.251 mol.) in 250 ml. of ethanol (nitrogen atmosphere) was added a solution of 50 g. (1.25 mol.) of sodium hydroxide in 100 ml. of water. The solution was allowed to reflux on a steam bath for 4 hr. after which the alcohol was removed by distillation. The alkaline reaction mixture was cooled and kept below 20° in an ice bath while ~30% sulfuric acid was added until the reaction was acid to nitrazine paper. The liberated mercaptan was extracted with 3 × 100 ml.-portions of methylene chloride. The combined methylene chloride extracts were washed with dilute sodium bicarbonate solution and dried over calcium chloride. After removal of the solvent, distillation gave 52.5 g. (82%) of product, b.p. 96–100°/1.5–1.7 mm. Redistillation yielded 48 g. (75%) of 1,3-di-(2-mercaptoethyl)-tetramethyldisiloxane, b.p. 94°/1.0 mm., n_{D}^{25} 1.4781.

Anal. Calcd. for $C_8H_{22}OS_2Si_2$: C, 37.74; H, 8.71; S, 25.19; Si, 22.07. Found: C, 37.28; H, 8.70; S, 25.36; Si, 21.82.

The infrared spectrum showed strong absorption at 1250 cm.$^{-1}$ ($>Si(CH_3)_2$ rocking vibration) and broad strong absorption at 1050–1090 cm.$^{-1}$ (Si-O stretching) and weak absorption at 2560 cm.$^{-1}$ (SH stretching vibration).

1,4-Dimercaptobutene-2. To a solution of *trans*-1,4-dibromobutene-2,[14] m.p. 53°, 162 g. (0.76 mol.) in 500 ml. of ethanol, was added rapidly a solution of 120 g. (1.52 mol.) of thiourea dissolved in about 300 ml. of 50% ethanol. Vigorous refluxing took place. Reflux was continued for 3 hr. and the solution was then cooled to 0°. There was obtained 178 g. (64% yield) of the di-isothiuronium salt, m.p. 225–227° (dec.).

In a 2-l. flask was placed a solution of 170 g. (0.46 mol.) of the di-isothiuronium salt dissolved in 800 ml. of water. While maintaining a nitrogen atmosphere, potassium hydroxide, 450 g. (~7.0 mol.) in 450 ml. of water, was added in one portion and the reaction was maintained at reflux temperature for 5 hr. At the end of this time, the solution was cooled and kept below 25° while 50% sulfuric acid was added until the reaction mixture was acid to Congo Red paper. The liberated dimercaptan was extracted with 3 × 200-ml. portions of methylene chloride. The combined extracts were washed with dilute sodium bicarbonate solution and dried over calcium chloride. Removal of the solvent and distillation of the residual oil gave only one small narrow boiling fraction, 7.5 g., b.p. 80–85°/18 mm. Redistillation gave 7.0 g. (13.4%) of 1,4-dimercaptobutene-2, b.p. 83°/17 mm., n_{D}^{25} 1.5608.

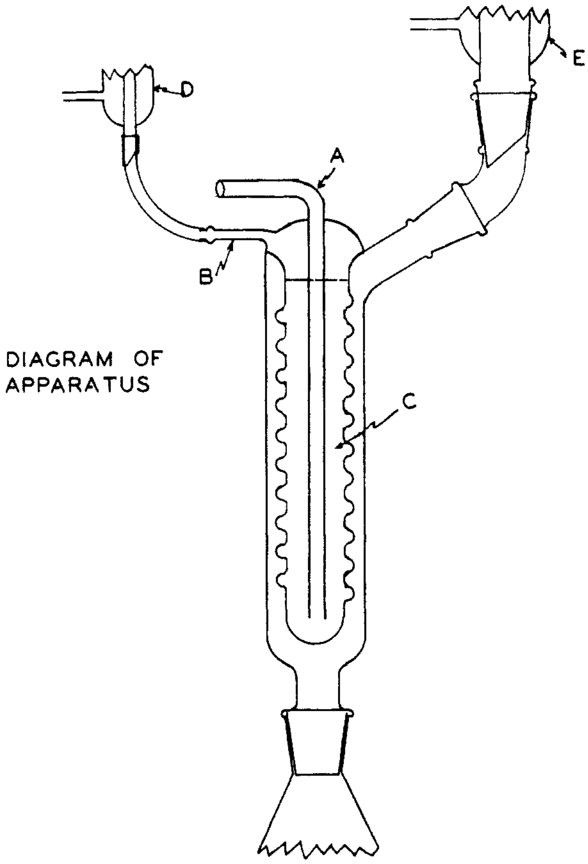

Fig. 1. Apparatus for oxidative polymerization at higher temperatures

Anal. Calcd. for $C_4H_8S_2$: C, 39.95; H, 6.70; S, 53.35. Found: C, 40.30; H, 6.41; S, 52.80.

Polymerization by Catalytic Air Oxidation. All oxidative polymerizations were carried out in a standardized emulsion recipe developed by Marvel and Olson.[5] The recipe is as follows:

Potassium hydroxide	8.0 g.
Lauric acid, C.P.	3.0 g.
Water	100 ml.
Selenous acid	50 mg.
Dithiol	10 ml.
Antifoam A (Dow-Corning)	1 drop

A convenient constant temperature reaction vessel for oxidations at higher temperatures was available in the conventional Friedrich's type condenser which is illustrated in Fig. 1. A unit batch of the emulsion containing the dithiol to be oxidized, C, *ca.* 115 ml., was placed in the water con-

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(14) C. Provost, *Compt. rend.*, **186**, 1209 (1928).

denser portion of the Friedrich's condenser. Filtered compressed air was bubbled through the inlet tube A at the rate of about 3–5 drops per second. The air outlet tube B was connected by means of "Tygon" tubing to an auxiliary vertical water condenser D which prevented the loss of water vapor from the heated solution. The dithiol emulsion undergoing oxidation was kept at constant elevated temperatures by refluxing vapors which were returned by condenser E. Liquids of suitable boiling points which were used as constant temperature baths were methylene chloride, 42°; acetone, 56°; ethanol (absolute), 78.4°; isopropyl acetate, 88.5°. Filtered compressed air was bubbled through the emulsions at a rate of between three to five drops per second for seven days. At the end of this time, the polymers were isolated by pouring the latex into about 1500 ml. of rapidly stirred methanol. The precipitated polymers were extracted with chloroform from a Soxhlet extractor whereupon most of the polymers went completely into solution (except some of IIIa prepared at 80° and above). The volume of chloroform solution was reduced to about 50 ml. and an equal volume of low boiling petroleum ether (b.p. 30–60°) was added to thin the viscosity and allow for better reprecipitation into about 1500 ml. of rapidly stirred methanol. The precipitated polymer was collected and dried in a vacuum oven at 60° for 24 hr.

a. *Polydisulfide of 1,3-Di-(2-mercaptoethyl)-tetramethyldisiloxane* (I). Analytical values for sulfur content of the soluble polydisulfides IIIa tended to be low in sulfur. Discrepancies became wider at the higher temperatures of formation.

b. *Polydisulfide of 1,3-Di-(3-mercaptopropyl)-tetramethyldisiloxane.* All the polydisulfides IIIb were completely soluble in chloroform. No variation was shown in analytical composition among polymers prepared over the temperature range investigated.

Preparation of Polypolysulfides. IIIa: To a solution of 6.0 g. (0.024 base mol.) of the polydisulfide of 1,3-di-(2-mercaptoethyl)-tetramethyldisiloxane (η = 0.428) in 100 ml. of chloroform was added a solution of 3.0 g. (0.094 g.-atom) of sulfur dissolved in carbon disulfide. The solvents were removed and the residue was maintained at 150–160° for 4 hr. (Note: Invariably hydrogen sulfide fumes were evolved to a greater or lesser degree as shown by lead acetate paper.) At the end of this time a high vacuum was applied for an additional hour to sublime out unreacted sulfur. On cooling the melt a solid dark brown rubbery polymer, 7.3 g. (95%), was obtained which was incompletely soluble in chloroform. The soluble portion (~10%) had an inherent viscosity of 0.145 (0.5% in chloroform).

Anal. Calcd. for $(C_8H_{20}OSi_2S_{3.49})_x$: C, 31.99; H, 6.78; Si, 18.71; S, 37.26. Found: C, 29.73; H, 6.04; Si, 19.80; S, 36.27.

IIIb: In an analogous manner, 9.0 g. (0.032 base mol.) of the polydisulfide from 1,3-di-(3-mercaptopropyl)-tetramethyldisiloxane (η = 0.627) was heated with 2.383 g. (0.075 g.-atom) of sulfur at 150–155° for 4 hr. followed by high vacuum for an additional hour. The polymer, 11.23 g. (93%), when cool was a dark rubbery solid, incompletely soluble in chloroform. The soluble portion had an inherent viscosity of 0.153 (0.5% in chloroform).

Anal. Calcd. for $(C_{10}H_{24}OSi_2S_{3.66})_x$: C, 35.97; H, 7.25; Si, 16.83; S, 35.16. Found: C, 34.57; H, 7.00; Si, 17.89; S, 34.44.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE GENERAL ELECTRIC COMPANY RESEARCH LABORATORY]

Alkylation of β-Cyanoethyltrichlorosilane and Preparation of β-Cyanoethyl(methyl)polysiloxanes

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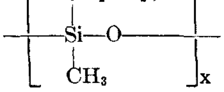
The reaction of equimolar amounts of β-cyanoethyltrichlorosilane, methylmagnesium bromide, and pyridine produced a mixture of the mono-, di-, and tri-methylated compounds. With methylzinc iodide (methyl iodide + zinc-copper couple) only β-cyanoethyltrimethylsilane was obtained, while dimethylcadmium gave only β-cyanoethyl(methyl)dichlorosilane. Hydrolysis of the dichlorosilane yielded β-cyanoethyl(methyl)polysiloxane oils. These oils do not undergo appreciable silicon-carbon cleavage either with bases or acids, in contrast to the α-cyano substituted polysiloxanes.

Many of the properties of the alkylpolysiloxanes, for example, their abnormally low boiling points and viscosity-temperature coefficients, are due to the low barrier to rotation about the Si—O bond and the consequent very low intermolecular forces in these molecules.[1] These properties can be altered significantly by the introduction of polar substituents into the hydrocarbon groups attached to the silicon atoms of the siloxane chains. The cyano group is among the more polar of these substituents and it has been shown that cyanomethyl groups attached to silicon bring about a large increase in the intermolecular forces, as measured by the activation energies for viscous flow and entropies of vaporization of a number of model silanes and siloxanes.[2] The cyanomethyl group, however, is readily cleaved from silicon by water, particularly in the presence of either acid or base.

$$\equiv SiCH_2CN + H_2O \longrightarrow \equiv SiOH + CH_3CN$$

This type of hydrolytic cleavage is characteristic of organosilicon compounds with electron-withdrawing groups on the carbon atom adjacent to silicon. It would be expected that compounds having a nitrile group on the β carbon would have approximately the same polar characteristics as the α substituted compounds, but might be more resistant to silicon-carbon cleavage. To test this hypothesis a β-cyanoethyl substituted polysiloxane,



$$\left[-\overset{CH_2CH_2CN}{\underset{CH_3}{Si}}-O- \right]_x$$

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(1) E. G. Rochow, *Chemistry of the Silicones*, 2nd edition, p. 115, John Wiley and Sons, New York, N. Y. (1951).

(2) M. Prober, *J. Am. Chem. Soc.*, **77**, 3224 (1955).