noncrystalline material present, but in this case most of the sample is crystalline. In both samples the noncrystalline phases have the same interchain distance, suggesting that these phases are very similar. Because of the magnitude of the interchain distance (9.4 Å) large pendant groups are probably on the polymer chain."

COLLEGE PARK, MD.

[CONTRIBUTION FROM THE MIDWEST RESEARCH INSTITUTE]

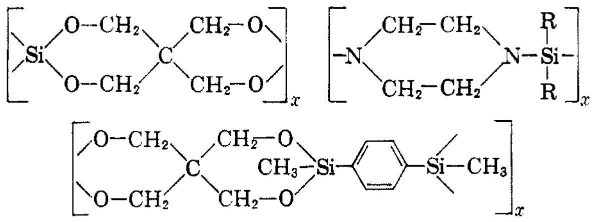
Reactions of Silanes with Pentaerythritol and Piperazine[1]

L. W. BREED, WILLIAM J. HAGGERTY, JR., AND JOHN HARVEY

Received January 7, 1960

Possible reactions for the preparation of linear polymers containing the alternate silane-pentaerythritol and silane-piperazine groups were investigated. Although prototype compounds were prepared by several procedures, attempted polymerization reactions failed to yield the desired polymers.

In the search for new polymer systems with good thermal stability, certain condensation products of silanes with pentaerythritol or piperazine could provide linear, rigid chains. For example:

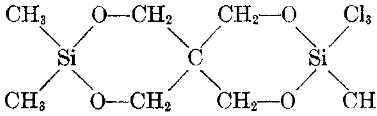


Several U. S. patents[2-4] report that the addition of pentaerythritol in varying amounts to silicone resins as a cross-linking agent gives resins which are superior to the unmodified resins, but no evidence was found that pentaerythritol has been used as an integral part of a silane polymer. In such a polymer, the absence of a β-hydrogen, as well as the rigidity of the chain, may contribute to thermal stability. No piperazine polymers containing silicon have been reported. The silicon-nitrogen bond is known to be very thermally stable if no hydrogen is attached to the nitrogen atom.[5] Polymers containing silicon-nitrogen bondings have been described by Cheronis.[6,7,8]

We obtained the prototype compound, 3,3,9,9-tetramethyl-2,4,8,10-tetraoxa-3,9-disilaspiro[5.5]-undecane by three procedures.

Procedure No. 1 was previously described by Davydova.[9] None of these syntheses is a high yield reaction likely to produce high molecular weight materials during polymerization.

1. $C(CH_2OH)_4 + 2(CH_3)_2Si(OAc)_2 \xrightarrow{61.5\%}$
2. $C(CH_2OAc)_4 + 2(CH_3)_2Si(OC_2H_5)_2 \xrightarrow[Al(OisoPr)_3]{40.4\%}$
3. $C(CH_2OH)_4 + 2(CH_3)_2Si(OC_2H_5)_2 \xrightarrow[p\text{-toluene-sulfonic acid}]{\text{low yield}}$



A fourth method used in the attempted preparation of dioxasilacyclohexane ring structure gave only a polymer. It is reported that chlorotrimethylsilane and pentaerythritol, in the presence of pyridine, gave a 90% yield of the tetrakistrimethylsilyl derivative.[10] However, when we treated pentaerythritol and dichloromethylphenylsilane in the presence of pyridine, a polymer rather than the bicyclic compound, 3,9-dimethyl-3,9-diphenyl-2,-4,8,10-tetraoxa-3,9-disilaspiro[5.5]undecane was obtained.

A portion of the polymer that flowed at 170° had a molecular weight of about 2000. The largest part, however, was benzene insoluble and could be drawn into fibers. The ratio of elements calculated from elementary analyses indicated that the amount of cyclization in the polymer was low.

Polymerization reactions generally resulted in the formation of insoluble and infusible products containing unchanged functional groups. The properties of the polymers suggest that a highly crosslinked structure is formed in preference to the

---

[1] This research was supported in whole or in part by the United States Air Force under Contract AF 33(616)-3675, monitored by the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio.

[2] J. E. Dereich, U. S. Patent **2,684,354** (July 29, 1954).

[3] J. T. Goodwin, Jr., U. S. Patent **2,686,740** (Aug. 17, 1954).

[4] J. L. Speier, U. S. Patent **2,576,486** (Nov. 27, 1951).

[5] R. R. McGregor, *Silicones and Their Uses*, McGraw-Hill Book Co., Inc., New York, 1954, p. 228.

[6] N. D. Cheronis, U. S. Patent **2,579,416** (Dec. 18, 1951).

[7] N. D. Cheronis, U. S. Patent **2,579,417** (Dec. 18, 1951).

[8] N. D. Cheronis, U. S. Patent **2,579,418** (Dec. 18, 1951).

[9] V. P. Davydova, and M. G. Voronkov, *Zhur. Obschei Khim.*, **28**, 1879 (1958).

[10] M. M. Sprung, *J. Org. Chem.*, **23**, 58 (1958).

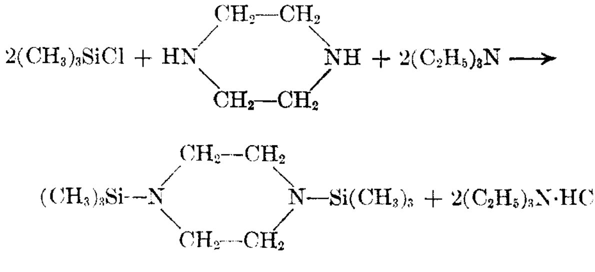
linear structure that would result if the reaction had produced a series of rings.

When ethyl orthosilicate and pentaerythritol tetraacetate were heated in cyclohexane in the presence of aluminum isopropylate, about 56% ethyl acetate was recovered in the distillate. A toluene soluble resin was obtained which formed a transparent brittle film on curing. Heated, the material gave visual evidence of decomposition between 250° and 320°. Elemental analyses indicated that the postulated polymer backbone had not been obtained and showed that the material contained a ratio of about two pentaerythritol groups per silicon atom.

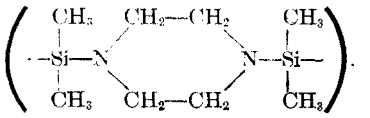
Treating pentaerythritol with silicon tetraacetate gave only a small amount of the expected acetic acid. The product, however, was insoluble in aromatic solvents.

When pentaerythritol tetraacetate and *p*-phenylenebis(diethoxymethylsilane) were condensed in the presence of a Lewis acid, only a 24% recovery of the theoretical ethyl acetate was obtained, but the resulting polymer was infusible and insoluble in benzene, toluene, and diethyl ether.

In studying the piperazine-silane system, no difficulty was encountered in the preparation of the prototype compound, *N*,*N*-bis(trimethylsilyl)-piperazine, by the dehydrohalogenation of the piperazine-chlorotrimethylsilane adduct with triethylamine, although the yield of the product was somewhat low (34%).



Attempts to prepare a polymer from piperazine and dichlorodimethylsilane gave a product containing distillable materials. The results of analyses for elements on the distillates from two experiments approximated the ratio of elements that would indicate a structure with two silane units for each piperazine unit. Although the properties of the two distillates were not identical—probably because of the different degree of hydration of the starting piperazine samples—the over-all degree of polymerization was low. The basic unit obtained by the reaction of equimolar quantities of dichlorodimethylsilane and piperazine had the structure:



EXPERIMENTAL[11]

3,3,9,9-Tetramethyl-2,4,8,10-tetraoxa-3,9-disilaspiro[5.5]-undecane. A 100-ml. round bottom flask equipped for distillation through a short Vigreux column was charged with 14.8 g. (0.1 mole) of diethoxydimethylsilane, 15.2 g. (0.05 mole) of pentaerythritol tetraacetate, 0.2 g. (0.001 mole) of aluminum isopropoxide, and 25 ml. of cyclohexane. While 75 ml. of the cyclohexane–ethyl acetate azeotrope was distilled from the mixture, constant volume was maintained by the addition of cyclohexane. When an insoluble material formed in the reaction flask and no more ethyl acetate was found in the distillate as determined by vapor phase chromatography, 50 ml. of toluene was added. The distillation was continued with the collection of additional ethyl acetate (total recovery—about 100%). The residue was distilled at atmospheric pressure and 5.0 g. (40.4%) of the product was obtained boiling 230–240°, m.p. 135° (reported,[9] m.p. 136°).

Anal. Calcd. for $C_9H_{20}O_4Si_2$: C, 43.50; H, 8.12. Found: C, 43.36; H, 8.17.

With Davydova's procedure, 0.30 mole of diacetoxydimethylsilane and 0.15 mole of pentaerythritol gave 61.5% of the same product boiling 243–260° (mostly between 243–245°).

When 17 g. (0.12 mole) of pentaerythritol, 34.0 g. (0.26 mole) of diethoxydimethylsilane, and 1 g. of *p*-toluenesulfonic acid were heated, ethanol distilled from the mixture. Distillation of the product, a viscous white mass, gave a small amount of the same material, melting at 130–132°.

Pentaerythritol and diethoxymethylphenylsilane. After a mixture of 17 g. (0.13 mole) pentaerythritol, 54.7 g. (0.26 mole) of diethoxymethylphenylsilane, and 1 g. of *p*-toluenesulfonic acid was heated at reflux for 3 hr., unchanged pentaerythritol was removed by filtration and a portion of the filtrate was heated at 110° for 72 hr. A flexible, elastic film was obtained.

Pentaerythritol and dichloromethylphenylsilane. To a stirred mixture of 27.2 g. (0.20 mole) of pentaerythritol and 126 g. (1.6 mole) of pyridine was added 76.4 g. (0.40 mole) of dichloromethylphenylsilane dropwise over a 1-hr. period with no attempt to control the temperature. In order to maintain stirring throughout the addition, several portions of anhydrous ether were added. When the product had cooled to room temperature, it was filtered and the filtrate was washed with several portions of ether. The combined filtrate and ether washings were concentrated by downward distillation to yield a soft, tacky residue. This residue was redissolved in ether and benzene, the solution was washed with water, and the solvents were again removed by distillation. After devolatilizing the residue for 3 hr. at 0.5 mm. and 140°, 56 g. of a tacky material remained which could be drawn into long fibers. Qualitative tests for nitrogen and chlorine were negative. The product was divided into two fractions by collecting the material which flowed through a hole in the bottom of an aluminum evaporating dish heated at 170°. The less fluid, benzene insoluble fraction, which constituted the major portion of the material, was labelled "A"; the other fraction, "B." The molecular weight of fraction B determined cryoscopically in benzene was 2,215 and 2,180. Empirical formulas, calculated from analysis for elements, are tabulated below.

Sample	C	H	Si	Empirical Formula
A	57.41	6.96	13.59	$C_{10.0}H_{14.4}O_{2.7}Si$
B	59.51	6.36	15.70	$C_{8.8}H_{11.3}O_{2.0}Si$

---

(11) All melting points and boiling points are uncorrected. Vapor phase chromatography was performed with a Perkin-Elmer 154B Vapor Fractometer. Elemental analyses were performed by Spang Microanalytical Labs., Ann Arbor, Mich.

Reaction of pentaerythritol and silicon tetraacetate. After 13.2 g. (0.05 mole) of silicon tetraacetate and 6.8 (0.05 mole) of pentaerythritol were heated at 120° for 2 hr., the acetic acid was distilled from the reaction mixture. Residual acetic acid was removed at room temperature with water aspirator vacuum. The weight loss was 5.5 g. (theory 12.0 g.) and only part of the residue toluene soluble. Evaporation of the solution of the soluble portion gave an oil which did not cure to a solid at 130°.

Reaction of pentaerythritol tetraacetate and ethyl orthosilicate. A mixture of 10.4 g. (0.05 mole) of redistilled ethyl orthosilicate, 15.2 g. (0.05 mole) of pentaerythritol tetraacetate, 0.2 g. of aluminum isopropylate, and 25 ml. of cyclohexane was heated to reflux and the cyclohexane–ethyl acetate azeotrope was removed at 73° until vapor phase chromatography indicated no more ester was being distilled. Toluene was added to the mixture and the distillation was continued; however only 56% of the theoretical ethyl acetate could be obtained. A film, formed by the evaporation of the solvent from the resin solution, was cured at 130° for several days and gave a transparent brittle solid which exhibited visual evidence of decomposition at 250–320°.

Anal. Calcd. for $C_5H_8O_4Si$ (the theoretical polymer): C, 37.48; H, 5.03; Si, 17.53. Found: C, 42.86; H, 5.95; Si, 8.50.

After 8-months' storage, the resin solution had gelled and additional ethylacetate had formed as indicated by odor.

Pentaerythritol tetraacetate and p-phenylenebis(diethoxymethylsilane). A mixture was prepared from 7.6 g. (0.025 mole) of pentaerythritol tetraacetate, 8.7 g. (0.024 mole) of *p*-phenylenebis(diethoxymethylsilane),[12] and 0.1 g. of ferric chloride. When this mixture was heated 20 hr. from 115° to 165°, the volatile products were collected in a Dry Ice trap. Vapor phase chromatographic analysis indicated that only 2.08 g. of ethyl acetate (23.5%) had been recovered. The polymer was infusible and insoluble in benzene, toluene, and diethyl ether.

N,N-bis(trimethylsilyl)piperazine. A stirred solution of 5 g. (0.06 mole) piperazine in 200 ml. of anhydrous ether was heated to reflux to dissolve the piperazine and then 12.6 g. (0.12 mole) of chlorotrimethylsilane was added dropwise. After the chlorosilane was added, 11.7 g. (0.12 mole) triethylamine was introduced. Filtration gave triethylamine hydrochloride (m.p. 254°) and a solution that was fractionally distilled to give 4.7 g. (34%) of *N,N*-bis(trimethylsilyl)-piperazine boiling at 210–216°.

Anal. Calcd. for $C_{10}H_{26}N_2Si_2$: C, 52.11; H, 11.37; N, 12.15; Si, 24.37. Found: C, 52.63; H, 10.85; N, 12.21; Si, 24.31.

Piperazine and dichlorodimethylsilane. Two attempts were made to prepare a polymer by the reaction of equimolar quantities of piperazine and dichlorodimethylsilane. Freshly distilled dichlorodimethylsilane and fresh anhydrous piperazine (Eastman, practical) were used.

After a stirred mixture of 20 g. (0.23 mole) of piperazine, 47 g. (0.46 mole) of triethylamine, and 750 ml. of anhydrous ether was heated to reflux, a solution of 30 g. (0.23 mole) of dichlorodimethylsilane in 200 ml. of anhydrous ether was added dropwise during 4 hr. Heating and stirring were continued for an additional 3 hr., and then the cooled mixture was filtered and the residue was washed with ether. The combined filtrate and washings were evaporated *in vacuo* yielding 39 g. of a reddish solid still containing some solvents. A portion of the product was purified by short path distillation, and about half the material was obtained as a white crystalline, moisture sensitive product boiling between 120–150° at 2–4 mm.

In a second experiment using a fresh lot of piperazine, a total of 84 g. of ether-insoluble solids separated. Evaporation of the ether gave 7.0 g. of a white solid, melting 105–115°, which distilled in a short path column mostly between 200–250° at 0.07 mm.

Anal. Calcd. for $C_8H_{20}Cl_2N_2Si_2$ (*N,N*-bis(chlorodimethylsilyl)piperazine): C, 35.41; H, 7.43; Cl, 26.13; N, 10.33; Si, 20.70. Found (1st experiment): C, 36.69; H, 8.08; Cl, 22.99; N, 9.92; Si, 21.98. Found (2nd experiment): C, 40.75; H, 8.69; Cl, 3.93; N, 11.52; Si, 24.00.

The ratio of elements in the first experiment is C, 7.8; H, 20.5; N, 1.8; Si, 2.0 and in the second experiment is C, 7.9; H, 20.2; N, 1.9; Si, 2.0 or equivalent to about one piperazine unit, $C_4H_8N_2$, to two silane units, $2C_2H_6Si$, in both cases.

KANSAS CITY 10, MO.

---

[12] L. W. Breed, F. Baiocchi, and C. Bolze, WADC TR 57-143, Part II, p. 20 (1957).