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# CARBORANE-SILOXANE ELASTOMERS

RMD Report 5065-F

Contract No. DA-11-070-AMC-852(W)

Report Period: 19 February 1965 through 18 February 1967

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## FOREWORD

This report was prepared by Thiokol Chemical Corporation, Reaction Motors Division, under U. S. Army Contract No. DA-11-070-AMC-852(W). It is a final report and covers work done over the period February 19, 1965 through February 18, 1967.

The work was administered under the direction of the Rock Island Arsenal, Rock Island Illinois, with Mr. Z. T. Ossefort as Project Engineer. Contributors at Thiokol were Mr. Nathan Mayes (Principal Investigator) and Mr. Alan Jackson. The work was under the general supervision of Dr. Murray S. Cohen and Mr. Joseph Green.

Presentations and publications that resulted from this work are:

(1) Thermal Stability of Carborane-Containing Polymers, by Joseph Green and Nathan Mayes, presented at the Symposium on High Temperature Polymers: Synthesis and Degradation, Western Regional Meeting, American Chemical Society, Los Angeles, California, November 18-20, 1965; published in the Journal of Macromolecular Science (Chemistry), Volume A1, Number 1, 1967, and in High-Temperature Polymers, edited by Charles L. Segal, Edward Arnold (Publishers) Ltd. London, Marcel Dekker, Inc., New York, 1967.

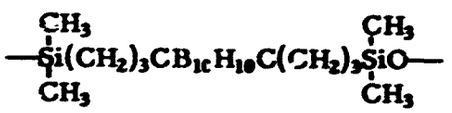
(2) Carborane Siloxane Polymers, by Nathan Mayes and Joseph Green, presented at the First Middle Atlantic Regional Meeting, American Chemical Society, Philadelphia, Pennsylvania, February 3-4, 1966.

(3) Carborane Polymers. IV. Polysiloxanes, by N. Mayes, J. Green, and M. S. Cohen, Journal of Polymer Science, Part A1, Volume 5, 365-379 (1967).

## ABSTRACT

**Toward the objective of synthesizing thermally stable elastomeric carborane-siloxane polymers, silane, carborane, and silane-carborane intermediates and monomers were prepared. Chlorosilanes, alkoxysilanes and a cyclic siloxane monomer were polymerized by heterogroup condensation, hydrolysis-condensation and ring-opening polymerization techniques. Polymers were obtained that ranged from viscous liquids and brittle solids to elastomeric gums depending on polymer molecular weight and structure.**

**Two types of polymer structures (I and II) were synthesized.**



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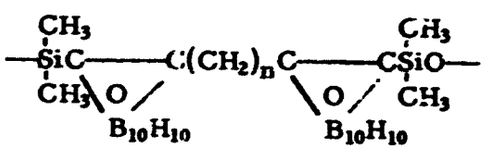

where n = 3 and 5

II

Polymers of structure I, of molecular weight 8,500 and higher, were elastomeric. Thermal stability evaluation by TGA and DTA indicated oxidative degradation at 240°C, no significant improvement over noncarborane polysiloxanes.

Polymer of structure II, where n=3, was nonelastomeric (mp 170-185°C), but TGA and DTA indicated this polymer to be stable to 350°C and oxidatively stable to 410°C. A polymer of similar structure, where n=5, had improved physical properties (slightly elastomeric gum) but lower thermal stability. Thermal analysis of this polymer indicated a nonoxidative decomposition at 250°C and an oxidative decomposition at 350°C.

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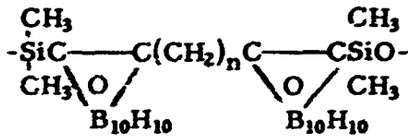
| 2. |  Structures | 17 |
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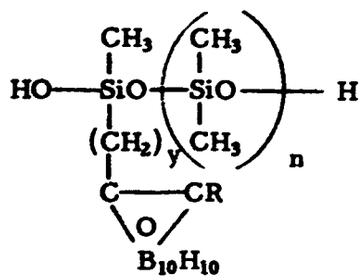
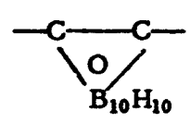
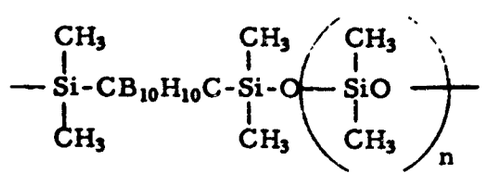
# I. INTRODUCTION

This work was undertaken to prepare carborane siloxane polymers that might be elastomeric and thermally stable. Previous efforts in this area have resulted in preparation of carborane siloxane polymers of structures I (Ref 1) and II (Ref 2).



where n = 0, 1, 3; y = 3, 4; R = H, $CH_3$;  = o-carborane

I



where n = 0, 1, 2, 3; $-CB_{10}H_{10}C-$ = m-carborane

II

Polymers of each type were elastomeric when the carborane units were sufficiently spaced to permit chain flexibility, and TGA data indicated thermal stability at temperatures above 400°C for some members of each type.

The efforts of the present program were directed toward the preparation of other carborane polysiloxane structures and evaluation of these as thermally stable elastomers. This required the preparation of carborane intermediates and carborane silane monomers, investigation of methods of polymerizing these materials, and finally thermal stability characterization of the resultant polymers.

# II. RESULTS

## A. Synthesis of Intermediates

### 1. Tetramethyldisiloxane

An attempt was made to prepare tetramethyldisiloxane by a Grignard reaction of methylmagnesium iodide with dichloromethylsilane followed by hydrolysis and fractional distillation of the products (Equation 1).

$$CH_3Si(H)Cl_2 + CH_3MgI \xrightarrow{(C_2H_5)_2O} [(CH_3)_2Si(H)Cl] \xrightarrow{H_2O} HSi(CH_3)_2OSi(CH_3)_2H \qquad (1)$$

A product of bp 70°C (bp of tetramethyldisiloxane is 71°C, Ref 3) was obtained in 15% yield. The product was iodine-colored and apparently impure. A second attempt using methylmagnesium bromide as methylating agent yielded 50% of colorless product of bp 72°C and $n_D^{20}$ 1.3694 (Lit. $n_D^{20}$ 1.3700, Ref 3). Proton nuclear magnetic resonance analysis indicated the product to be tetramethyldisiloxane; however, infrared analysis and quantitative analysis for SiH indicated the presence of an impurity which was not identified.

### 2. Chlorodimethylsilane

An effort was made to prepare chlorodimethylsilane by silicon halide-silicon hydride interchange reaction as suggested by Eaborn (Ref 4). Eaborn cites an example of silicon halide-silicon hydride interchange in which chlorodiethylsilane is obtained from the aluminum chloride catalyzed reaction of triethylsilane and dichlorodiethylsilane, and he suggests that a similar reaction could occur using the polysiloxane $\left[\begin{matrix} CH_3 \\ SiO \\ H \end{matrix}\right]_x$ as a hydrogen source in place of triethylsilane. The suggested approach is attractive for the preparation of chlorodimethylsilane because of the ready availability of the hydrogen source (hydrolysis of $Cl_2Si(CH_3)H$) and because the product should be easily isolated. The reaction was attempted as suggested, however, none of the desired product was obtained (Equation 2).

$$Cl_2Si(CH_3)_2 + \left[\begin{matrix} CH_3 \\ SiO \\ H \end{matrix}\right]_x \xrightarrow[AlCl_3,\ reflux,\ 10\ hr]{} ClSi(CH_3)_2H \qquad (2)$$

The preparation of chlorodimethylsilxane was accomplished by reduction of dichlorotetramethyldisiloxane with lithium aluminum hydride. It has been reported in several instances that partial reduction of organohalogensilanes is not possible (Ref 5). Thus, one cannot expect to reduce dichlorodimethylsilane to chlorodimethylsilane. Such reactions actually yield the fully-reduced silane even when a considerable deficiency of lithium aluminum hydride is used (Equation 3).

$$Cl_2Si(CH_3)_2 + LiAlH_4 \longrightarrow H_2Si(CH_3)_2 + Cl_2Si(CH_3)_2 \qquad (3)$$

A variation of this reaction was done here in which the dichlorodimethylsilane was first partially hydrolyzed to dichlorotetramethyldisiloxane and then reduced with lithium aluminum hydride in ether solution. Reduction occurred preferentially at the siloxane bonds to yield chlorodimethylsilane (Equation 4).

$$\begin{aligned} Cl_2Si(CH_3)_2 + H_2O &\longrightarrow ClSi(CH_3)_2OSi(CH_3)_2Cl \\ ClSi(CH_3)_2OSi(CH_3)_2Cl + LiAlH_4 &\xrightarrow{\text{ether}} ClSi(CH_3)_2H \end{aligned} \qquad (4)$$

The product (bp 36°C) could not be separated from ether by distillation, but its presence in the distilled ether solution (bp 35°C) was indicated by the infrared spectrum which exhibited absorptions for SiH and $SiCH_3$. The solution yielded acid on hydrolysis, and a titration, assuming all chlorosilane present to be chlorodimethylsilane, indicated that the latter had formed in 53% yield (based on lithium aluminum hydride). If reduction also occurred at silylchloride bonds the formation of dimethylsilane would be expected; however, no dimethylsilane was obtained in the reaction products.

When the reaction was conducted using, instead of pure dichlorotetramethyldisiloxane, a mixture of dichlorosiloxanes obtained from the partial hydrolysis of dichlorodimethylsilane there was copious evolution of dimethylsilane. Chlorodimethylsilane also formed as it had previously; however, it was noted that distillation of the chlorodimethylsilane-ether solution proceeded smoothly at pot temperatures <75°C, but at higher pot temperatures, a reaction occurred to yield dimethylsilane (Equation 5).

$$\begin{array}{ccccc} Cl_2Si(CH_3)_2 + H_2O & \longrightarrow & ClSi(CH_3)_2(OSi(CH_3)_2)_nCl & & \\ & & n = 0, 1, 2, 3, 4, & & \\ & & \downarrow \; LiAlH_4, \text{ ether} & & \\ H_2Si(CH_3)_2 & \xleftarrow{>75^\circ C} & ClSi(CH_3)_2H + H_2Si(CH_3)_2 & & \end{array} \qquad (5)$$

The latter reaction was apparently a disproportionation between chlorodimethylsilane and hydrosiloxanes still present in the reaction mixture.

### 3. 1,7-Diallylcarborane

1,2-Diallylcarborane, an isomer of the subject compound, was previously prepared (Ref 6) and the same procedure was used here to synthesize the 1,7 isomer. m-Carborane was a starting material in this synthesis. It was prepared in a series of steps involving o-carborane preparation by oxidation of 1,2-bis(hydroxymethyl)carborane (Ref 7) and finally thermal isomerization of o-carborane to m-carborane (Ref 8). m-Carborane was converted to the diallyl compound by reactions illustrated in Equations 6 and 7.

$$HCB_{10}H_{10}CH + 2BuLi \longrightarrow LiCB_{10}H_{10}CLi + 2BuH \qquad (6)$$

$$LiCB_{10}H_{10}CLi + 2CH_2{=}CHCH_2Br \longrightarrow CH_2{=}CHCH_2CB_{10}H_{10}CCH_2CH{=}CH_2 \qquad (7)$$

The reactions progressed smoothly to yield 89-92% of distilled product (yield based on m-carborane). The product is a colorless liquid of bp 63°C/0.15 mm and $n_D^{20}$ 1.5335. It was characterized by infrared and elemental analysis.

Calculated for $C_8H_{20}B_{10}$: C, 42.82; H, 8.98; B, 48.18.

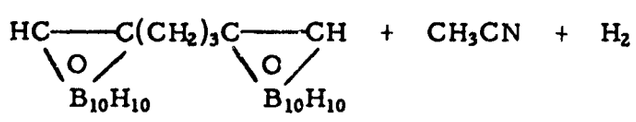
Found: C, 42.72; H, 8.87; B, 48.17.

### 4. 1,3-Di-o-carboranylpropane

The compound, 1,3-di-o-carboranylpropane was prepared according to equations 8 and 9.

$$B_{10}H_{14} + CH_3CN \xrightarrow[\text{Reflux}]{CH_3CN} (CH_3CN)_2B_{10}H_{12} + H_2 \qquad (8)$$

$$(CH_3CN)_2B_{10}H_{12} + HC{\equiv}C(CH_2)_3C{\equiv}CH \xrightarrow[\text{Reflux}]{CH_3CN} \qquad (9)$$




The product, which was obtained in low yield, was a crystalline solid of mp 346 - 48°C. It was identified by infrared and elemental analyses.

Analysis Calculated for $C_7H_{28}B_{20}$: C, 25.6; H, 8.6; B, 65.8

Found: C, 26.7; H, 9.3; B, 66.6

An attempt was made to thermally isomerize 1,3-di-o-carboranylpropane to the meta isomer, 1,3-di-m-carboranylpropane. The effort to prepare the meta derivative in this manner was prompted by the successful isomerization of methyl-o-carborane to methyl-m-carborane in 69% yield (Ref 9). Pyrolysis of di-o-carboranylpropane at 450°C for 24 hours yielded material of mp 295- 306°C which showed changes in the infrared spectrum indicative of isomerization to a m-carborane species. However, all attempts to isolate a pure component from the crude pyrolysis product have failed.

5. 1,4-Di-o-carboranylbutane

An attempt to prepare 1,4-di-o-carboranylbutane by the same procedure used to prepare the propane derivative failed to yield the desired product. Modification of the procedure, with the use of diethylsulfide-decaborane as carboranylating agent and toluene as solvent, led to a 10% yield of material of mp 281-283°C. It was identified by infrared and elemental analyses as 1,4-di-o-carboranylbutane.

Calculated for $C_8H_{30}B_{20}$: C, 28.04; H, 8.83; B, 63.12

Found: C, 28.20; H, 8.89; B, 62.91

The low yields obtained prompted further investigation of the carboranylation reaction as well as alternate means of preparation.

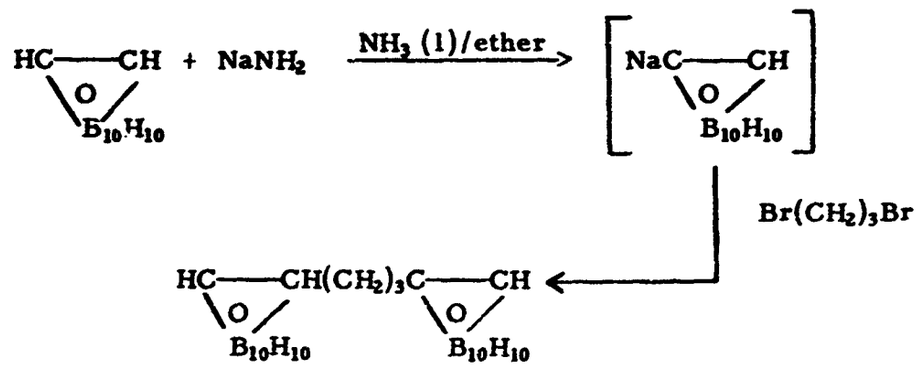
In attempts to improve the yields, we found that altering reaction conditions such as reactant ratio, reaction time, solvent, and temperature did not substantially increase the yield. Difficulty in the carboranylation of diacetylenic compounds has been reported by Hawthorne (Ref 10), who determined that isolation of the monocarboranylated intermediate followed by further carboranylation to the desired product resulted in significantly higher yields. This approach was tried here for the preparation of 1,4-di-o-carboranylbutane. We found, however, that even the monocarboranylated product was formed in low yield and that the reaction was accompanied by gas evolution of the same order of magnitude as the yield. This showed that the low yields are not due to sluggish reaction of the second acetylenic group (see Section II.A.6. for further discussion of yields).

In the course of this work, a new compound, the monocarboranylated product, 6-o-carboranylhex-1-yne, was isolated. It was distilled as a colorless liquid ($n_D^{20}$ 1.5401) at 114°/0.17 mm. It was identified by its infrared spectrum (Figure 1) and elemental analysis.

Analysis Calculated for $C_8H_{20}B_{10}$: C, 42.81; H, 8.98; B, 48.21

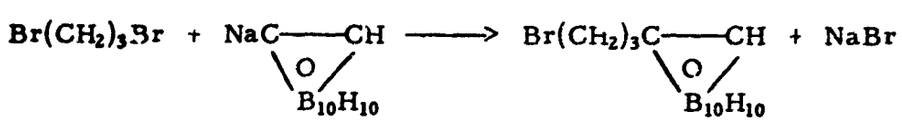
Found: C, 44.18; H, 9.27; B, 47.45

The alternate procedure investigated for the preparation of dicarboranylalkanes was based on Zakharkin's reported alkylation of mono- and dimetallo carborane derivatives (Ref 11). We attempted to use this type of alkylation to prepare a di-o-carboranylalkane according to Equation 10.

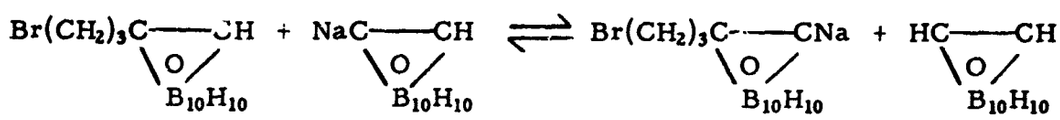



(10)

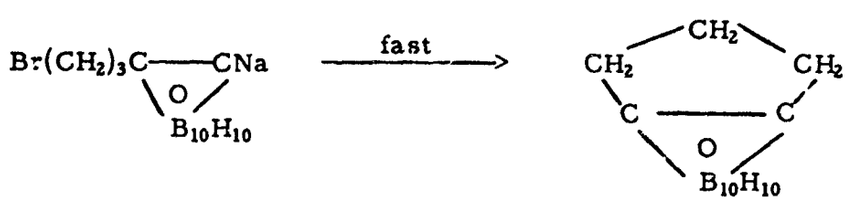
According to the literature, the intermediate monometallo carborane would form in at least 66% yield under the conditions used, and we expected that this would react as indicated in Equation 10. The product isolated from the reaction proved to be the cyclic 1,2-o-carboranylcyclopentane (Ref 12). It forms, apparently, because a transmetalation equilibrium exists between metalated carborane and carborane having a free hydrogen. The equilibrium, as illustrated in Equations 11-13, is driven to the right in this case because a low energy path to cyclic formation exists.




(11)




(12)




(13)

The preparation of di-m-carboranylalkanes through alkylation of sodio-m-carborane was investigated. The reactions attempted were 1-sodio-m-carborane with 1,3-dibromopropane and with 1,4-dibromobutane. The m-carborane derivatives would not be expected to cyclize as did the o-carborane compounds. The reactions did not yield the desired dicarboranylalkanes, instead

products that appear to be low polymers were obtained. One such product that was isolated and analyzed by infrared spectroscopy and elemental analysis is apparently either $HCB_{10}H_{10}C(CH_2)_3CB_{10}H_{10}C(CH_2)_3CB_{10}H_{10}CH$ or $HCB_{10}H_{10}C(CH_2)_3[CB_{10}H_{10}C(CH_2)_3]_2CB_{10}H_{10}CH$. No solvent for this material could be found, hence molecular weights could not be determined.

| | | | |
|---|---|---|---|
| Analysis Calcd. for $C_7H_{28}B_{20}$: | C, 25.5; | H, 8.62; | B, 65.8. |
| $C_{12}H_{44}B_{30}$: | C, 28.1; | H, 8.65; | B, 63.2. |
| $C_{17}H_{60}B_{40}$: | C, 29.3; | H, 8.69; | B, 62.0. |
| Found: | C, 27.9; | H, 8.58; | B, 61.5. |

6. 1,5-Di-o-carboranylpentane

Carboranylation of 1,8-nonadiyne was accomplished by reaction of the diyne with bis(diethylsulfido)decaborane, prepared in situ from decaborane and diethylsulfide in toluene as solvent. Reaction at toluene reflux for either 24 hours or 288 hours yielded 8.5% of dicarboranyl product. Isolation of the product from the reaction mixture involved evaporating the solvent, treatment of the residue with caustic to decompose noncarborane boron hydrides and extraction of the carborane product with heptane. The heptane extract was a mixture of solid and liquid products which were separated by distilling off the liquid at 110°C/0.05 mm. The residue was recrystallized from heptane and then from acetic acid to obtain crystals of mp 179-180°C. The infrared spectrum (Figure 2) indicated this to be the dicarboranylalkane.

The distilled liquid is a saturated alkyl carborane, probably heptylcarborane. This is indicated by the infrared spectrum (Figure 3) and the boiling temperature, both of which are similar to those of hexylcarborane. The isolation of this compound suggests that side reactions occurred in which acetylenic compounds were hydrogenated either by the hydrogen released during carborane formation or by boron hydride byproducts of the reaction. Support for this view is found in the preparation of isopropylcarborane by the reaction of isopropenylcarborane with the solid byproduct obtained from the preparation of isopropenylcarborane from decaborane, acetonitrile, and isopropenylacetylene (Ref 13). The low yields of dicarboranylalkane product and the low gas evolution observed during the reaction are accounted for (at least in part) by this side reaction.

7. m-Carborane

m-Carborane, until now, has been synthesized only by thermal isomerization of o-carborane. The synthesis generally employed for o-carborane is a multistep process involving the reaction of decaborane with butynediacetate, hydrolysis of that product to a diol, and oxidation of the diol to o-carborane (Ref 7). We investigated the preparation of m-carborane by the pyrolysis and isomerization of an alkyl carborane, isopropyl-o-carborane.

The pyrolysis of isopropyl-o-carborane was studied using an apparatus consisting of a 200 ml. Pyrex flask in which the isopropyl-o-carborane was vaporized, a quartz tube (18 x 1 in.) which was heated by a furnace and through which the vapors passed, and a Pyrex collection flask in which the vapors were condensed. The apparatus was first thoroughly flushed with nitrogen and then the carborane compound heated at 270-280°C with a metered flow of nitrogen to carry the vapors into the heated tube.

The initial experiments, conducted with an unpacked tube at 600-725°C determined that pyrolysis did yield m-carborane as a product; however, the conversion was low under the conditions employed. In subsequent experiments the use of a packed tube (quartz fragments as packing), a low nitrogen flow (20 ml. / min.), and a tube temperature (outside wall) of 670°C increased the conversion to 50% at a throughput of 14 g/hour. The carborane was obtained in a mixture with some brown unidentified byproduct from which the carborane was separated by sublimation. The conversion figure is for the crude sublimed product which was purified with small loss by recrystallization from acetic acid. Recrystallized products melted at 266-70°C, and an infrared spectrum of the product indicated that it was pure m-carborane.

A sample of the volatile byproduct of the pyrolysis was collected at liquid nitrogen temperature and analyzed by infrared spectroscopy. The spectrum was identical to that of methane and indicated the presence of no other hydrocarbons. This suggests that methyl radicals produced in the pyrolysis are more able to combine with hydrogen radicals than with other methyl or alkyl radicals and suggests that there is an abundance of hydrogen radicals available for combination. These hydrogen radicals probably result from partial decomposition of carborane.

8. Attempted Synthesis of 1, 5-Di-m-carboranylperfluoropentane

The synthesis of the subject compound was expected to parallel the recently reported synthesis of perfluoro-1, 6-diphenylhexane, illustrated in equation 14 (Ref 14).

$$C_6F_5Br + Mg \longrightarrow C_6F_6MgBr \xrightarrow[\text{ether}]{ClOC(CF_2)_4COCl} C_6F_5\overset{O}{\overset{\|}{C}}(CF_2)_4\overset{O}{\overset{\|}{C}}C_6F_5 \xrightarrow{SF_4} C_6F_5(CF_2)_6C_6F_5 \text{(m.p. 59.5-60°C)} \qquad (14)$$

The synthesis was first attempted with 1-sodio-m-carborane and perfluoroglutaryl chloride. The 1-sodio-m-carborane was prepared by treating carborane with sodium amide in refluxing toluene. This procedure, when used with o-carborane, has been reported to give the monosodio derivative in goold yield (Ref 15). The formation of 1-sodio-m-carborane was indicated by ammonia evolution; it was not isolated but was reacted in situ with the acid chloride. This reaction was largely incomplete and was complicated by the presence of sodium amide which also reacted with acid chloride. The major product obtained, after hydrolysis of the reaction mixture, was m-carborane, which resulted from hydrolysis of unreacted sodio-m-carborane. The only other product isolated was $HCB_{10}H_{10}CC(CF_2)_3CNH_2$. The course of the reaction, as shown in equation 15, indicated that a more reactive metallo-carborane species was desirable, and elimination of other organometallic species from the reaction mixture was necessary.

$$HCB_{10}H_{10}CH + NaNH_2 \xrightarrow[\text{Reflux}]{\text{Benzene}} NaCB_{10}H_{10}CH + NH_3$$

$$NaCB_{10}H_{10}CH + Cl\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}Cl + NaNH_2 \longrightarrow HCB_{10}H_{10}C\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}NH_2 \qquad (15)$$

For these reasons the reaction was next attempted with lithio-m-carborane which was prepared from n-butyllithium and excess m-carborane. An excess was used to insure formation of monolithio derivative and to minimize unreacted butyllithium. This reaction yielded two products after separation of excess m-carborane. An ether insoluble portion, representing 65% of the product, did not melt below 325°C and was partially soluble in acetone, methanol and acetic acid. It was fully soluble in dimethylformamide. The infrared spectrum (Figure 4) exhibited absorption bands at 3.9 microns for BH of m-carborane, at 5.9 microns for ketone carbonyl, and in the 8-9 micron region for $CF_2$. The spectrum suggests the presence of the desired material; however, no means was found for isolating this material.

An ether soluble portion melted with decomposition at 85-120°C. The infrared spectrum of this product (Figure 5) was similar to the spectrum of the other product, except for bands at 5.78 microns and 5.98 microns, which are apparently due to different types of keto carbonyls. Both materials exhibit absorption bands in the region of 3.0-3.2 which may be for OH. This suggests that reaction, as illustrated in equation 16, may have occurred.

$$HCB_{10}H_{10}C\overset{O}{\overset{\|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}CB_{10}H_{10}CH + HCB_{10}H_{10}CLi \longrightarrow \xrightarrow{H_2O}$$

$$(HCB_{10}H_{10}C)_2\overset{OH}{\overset{|}{C}}(CF_2)_3\overset{O}{\overset{\|}{C}}CB_{10}H_{10}CH + LiOH \qquad (16)$$

The reaction was attempted again using the Grignard derivative, m-carboranylmagnesium bromide. This was prepared by reaction of m-carborane with ethyl magnesium bromide in tetrahydrofuran solution. Perfluoroglutaryl chloride was added to the Grignard solution and stirred at room temperature for one hour. The formation of solids indicated the reaction occurred; however, upon hydrolysis the only product recovered was m-carborane.

The reaction was repeated with m-carboranylmagnesium iodide and perfluoroglutaryl chloride; however, again the only product recovered was m-carborane.

B. Synthesis of Monomers

1. 1,7-Bis(chlorodimethylsilylpropyl)-m-carborane

Chlorodimethylsilane, in ether solution, was allowed to react with 1,7-diallylcarborane (Equation 17), in the presence of chloroplatinic acid. Distillation of the reaction mixture yielded a small quantity of unreacted 1,7-dial-

$$ClSi(CH_3)_2H + CH_2{=}CHCH_2CB_{10}H_{10}CCH_2CH{=}CH_2 \xrightarrow[\text{Ether}]{H_2PtCl_6\cdot 6H_2O} \quad (17)$$

$$Cl\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}(CH_2)_3CB_{10}H_{10}C(CH_2)_3\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{Si}}Cl$$

lylcarborane and fractions that boiled at 135°C/0.04 mm and 155°C/0.05 mm. The infrared spectrum of the lower boiling fraction indicated it to be the partial addition product, $H_2C{=}CHCH_2CB_{10}H_{10}C(CH_2)_3Si(CH_3)_2Cl$. The higher boiling material was, on the basis of infrared, NMR, and elemental analyses, identified as 1,7[bis(3-chlorodimethylsilyl)propyl] carborane.

Calculated for $C_{12}H_{34}B_{10}Cl_2Si_2$: C, 34.84; H, 8.29; B, 26.16; Cl, 17.83; N.E. 206.8.

Found: C, 34.18; H, 8.85; B, 25.94; Cl, 17.17; N.E. 209.8.

2. 1,7-Bis(methoxydimethylsilylpropyl)-m-carborane

The preparation of 1,7-bis(methoxydimethylsilylpropyl)-m-carborane was attempted first by the reaction of 1,7-bis(chlorodimethylsilylpropyl)-m-carborane with excess methanol after the analogous procedure to prepare 1,7-bis(methoxydimethylsilyl)-m-carborane (Ref 16). Our efforts produced siloxanes that apparently resulted from reaction of the chlorosilane (or methoxysilane) with water formed from the reaction of byproduct hydrogen chloride with excess methanol (Ref 17).

Modification of the reaction conditions to use methyl orthoformate instead of methanol resulted in the preparation of 1,7-bis(methoxydimethylsilylpropyl)-m-carborane which was obtained as a colorless liquid of bp 142-150°C at 0.02 mm (Equation 18).

$$Cl\overset{CH_3}{\underset{CH_3}{Si}}(CH_2)_3CB_{10}H_{10}C(CH_2)_3\overset{CH_3}{\underset{CH_3}{Si}}Cl + 2(CH_3)_3CH \longrightarrow \tag{18}$$

$$CH_3O\overset{CH_3}{\underset{CH_3}{Si}}(CH_2)_3CB_{10}H_{10}C(CH_2)_3\overset{CH_3}{\underset{CH_3}{Si}}OCH_3 + HCOOCH_3 + 2CH_3Cl$$

Calculated for $C_{14}H_{40}B_{10}Si_2O_2$: C, 41.54; H, 9.96; B, 26.71; Si, 13.88.

Found: C, 41.00; H, 10.73; B, 26.4; Si, 11.11.

3. 1-Oxa-2,12-disila-2,2,12,12-tetramethyl-6,7,8-(1,7-m-carboranylene)cyclodecane

Hydrolysis of 1,7-bis(chlorodimethylsilyl)propyl m-carborane yielded a crystalline product which is a 12-membered m-carborane exocycle (Equation 19).

$$Cl\overset{CH_3}{\underset{CH_3}{Si}}(CH_2)_3CB_{10}H_{10}C(CH_2)_3\overset{CH_3}{\underset{CH_3}{Si}}Cl + H_2O \longrightarrow \left[O\overset{CH_3}{\underset{CH_3}{Si}}(CH_2)_3CB_{10}H_{10}C(CH_2)_3\overset{CH_3}{\underset{CH_3}{Si}}\right] \tag{19}$$

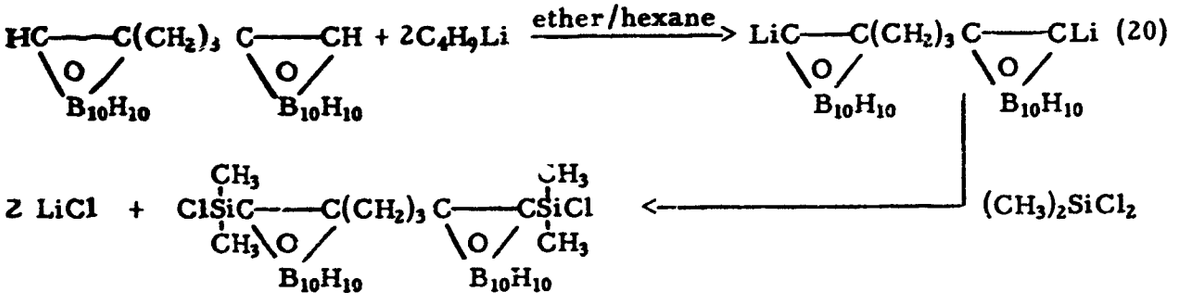
The crystalline product was obtained in small yield (<10%) on bulk hydrolysis of the silane; however, yields increased to 45% upon use of acetone as solvent. The remaining portion of hydrolysis product was linear polymer. The crystalline material was isolated by sublimation at 180-230°C/0.04 mm Hg. The sublimed product was recrystallized from acetone-chloroform to yield white needle crystals of mp 176.5°C. A mass spectrographic analysis showed a m/e peak at 284 which could be for the fragment, $\overset{CH_3}{\underset{CH_3}{Si}}(CH_2)_3CB_{10}H_{10}C(CH_2)_3$. No parent peak was noted. Infrared analysis supported the proposed structure with absorption peaks at 2930 $cm^{-1}$ for the $CH_2$, at 2600 $cm^{-1}$ for BH, at 1250 $cm^{-1}$ for $SiCH_3$, at 1175 $cm^{-1}$ for $Si(CH_2)_3CB_{10}H_{10}C$, and at 1052 $cm^{-1}$ for Si-O-Si. A molecular weight determination by the cryoscopic method and elemental analysis confirmed the structure.

Calculated for $C_{12}H_{34}B_{10}OSi_2$: C, 40.18; H, 9.55; B, 30.14; Si, 15.66; mol. wt. 358.

Found: C, 40.20; H, 9.89; B, 30.00; Si, 16.57; mol. wt. 377.

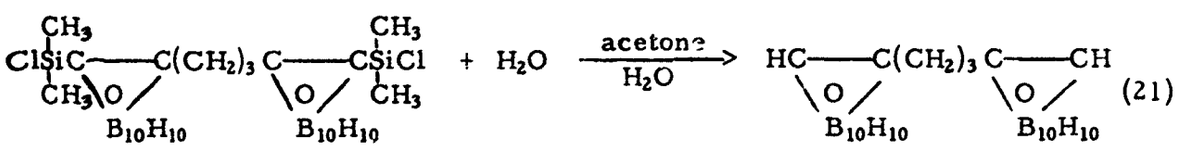
4. 1, 3-Bis(1-chlorodimethylsilyl-o-carboran-2-yl)propane

This was prepared by treating the dilithio derivative of 1, 3-di-o-carboranylpropane with a large excess of dichlorodimethylsilane (Equation 20).



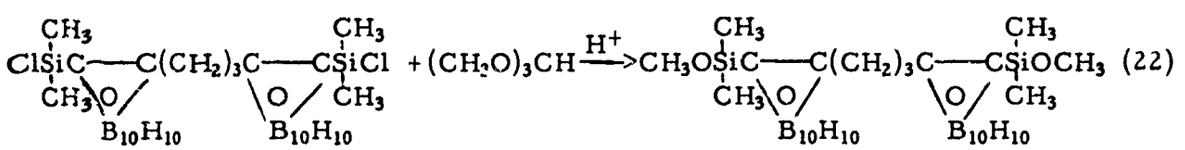
The product was obtained in 72% yield as a solid of mp 210-211°C. It was identified by its infrared spectrum (Figure 6) and neutralization equivalent. Neutralization equivalent calculated: 156.8; found 157.9.

The compound hydrolyzed when treated with acetone and water, resulting in cleavage of the silicon-carborane bond and formation of the original di-o-carboranylalkane (Equation 21).



5. 1, 3-Bis(1-methoxydimethylsilyl-o-carboran-2-yl)propane

The methoxy derivative was prepared by the acid (hydrochloric or p-toluene-sulfonic) catalyzed reaction of trimethoxymethane and bis(1-chlorodimethylsilyl-o-carboran-2-yl)propane (Equation 22).



The product, recovered in 60% yield after recrystallization from methanol, melted at 156-158°C. A sample recrystallized from pentane melted at 159.5-160°C. This methoxy compound was identified by infrared spectroscopy (Figure 7).

As previously noted for the chloro derivative, the methoxy compound hydrolyzed when treated with acetone and water with cleavage occurring at the silicon-carborane bond.

6. 1,5-Bis(1-chlorodimethylsilyl-o-carboran-2-yl)pentane

This material was synthesized in the manner described above for the propane derivative. The crude yield of silylated carborane product was 87.8%. This product, in contrast to 1,3-bis(1-chlorodimethylsilyl-o-carboran-2-yl)-propane, was not effectively purified by recrystallization from heptane; however, it was recrystallizable from diethoxydimethylsilane and, after washing with Freon 113, was obtained as crystals of mp 139.5-141°C. The infrared spectrum (Figure 8) was almost identical to that of the propane derivative.

7. 1,5-Bis(1-methoxydimethylsilyl-o-carboran-2-yl)pentane

The methoxy derivative was prepared by reaction of 1,5-bis(1-chlorodimethylsilyl-o-carboran-2-yl)pentane with excess trimethoxy methane using anhydrous hydrogen chloride as catalyst. The product, after a single recrystallization from methanol, was obtained as white crystals, mp 106-110°C, in 40% yield. The infrared spectrum (Figure 9) exhibits an absorption at 9.2 microns, which is indicative of the SiOC bonding of the methoxy derivative.

C. Synthesis of Polymers

1. $-\underset{CH_3}{\overset{CH_3}{Si}}(CH_2)_3CB_{10}H_{10}C(CH_2)_3\underset{CH_3}{\overset{CH_3}{Si}}O-$ Structures

a. Silyl Hydride Addition Polymerization

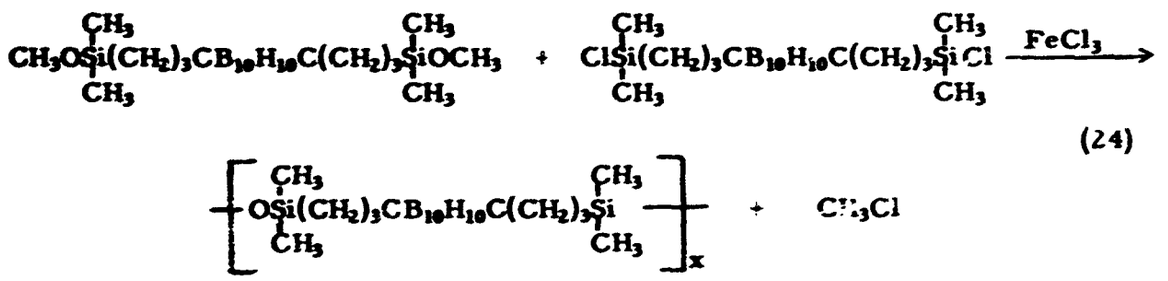
The preparation of polymer by the reaction of tetramethyldisiloxane and 1,7-diallylcarborane was investigated (Equation 23).

$$H\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}H + H_2C{=}CHCH_2B_{10}H_{10}CCH_2CH{=}CH_2 \xrightarrow[\text{Ether, reflux}]{H_2PtCl_6\cdot 6H_2O} \left[ -\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}(CH_2)_3CB_{10}H_{10}C(CH_2)_3- \right]_x \quad (23)$$

There was an exothermic reaction upon mixing the reactants in the presence of chloroplatinic acid. The product, obtained after refluxing in ether several hours, was a thin liquid apparently of low molecular weight. The infrared spectrum showed loss of SiH and C=C and indicated that addition had taken place; however, this type of polymerization did not appear to merit further investigation.

b. Alkoxysilane-Halosilane Condensation

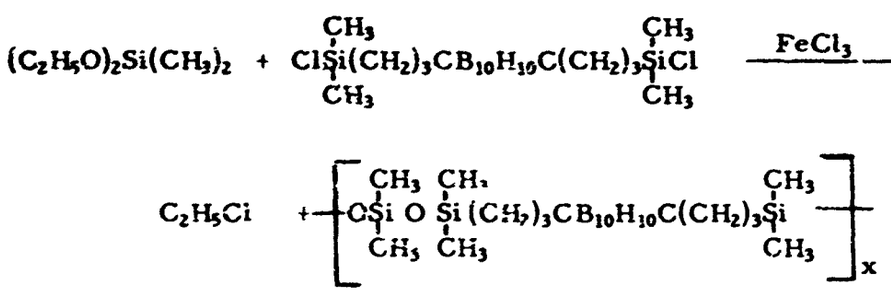
The alkoxysilane-halosilane condensation polymerization allows the preparation of copolymers of a definite and alternating structure. This method was thus used to prepare polysiloxanes in which the ratio of carborane moieties to siloxane moieties could be varied. A polymer containing these moieties in 1:1 ratio was prepared by the condensation of 1,7-bis(methoxydimethylsilylpropyl)-m-carborane and 1,7-bis(chlorodimethylsilylpropyl)-m-carborane as illustrated in equation 24.



(24)

This reaction was conducted at temperatures up to 230°C using ferric chloride as catalyst; however, there was difficulty in obtaining complete reaction. This was evidenced by the evolution of only 70% of the theoretical quantity of methyl chloride and the apparent low molecular weight of the product which was obtained as a viscous liquid.

Similarly, the preparation of polymer with carborane to siloxane in 1:2 ratio by reaction of 1,7-bis(chlorodimethylsilylpropyl)-m-carborane and diethoxydimethylsilane resulted in liquid polymer of 1800 molecular weight (Equation 25).

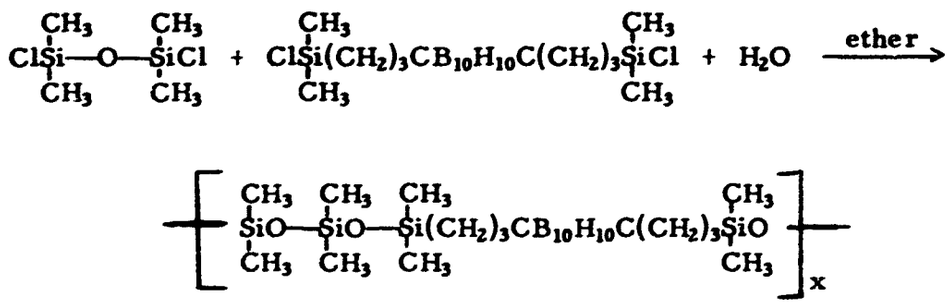


(25)

c. Hydrolysis-Condensation

Hydrolysis of 1,7-bis(chlorodimethylsilylpropyl)-m-carborane yielded an elastomeric gum polymer of 5200 molecular weight and the cyclic compound described above under "Monomer Synthesis". The gum was obtained in up to 90% yield by conducting the reaction without solvent.

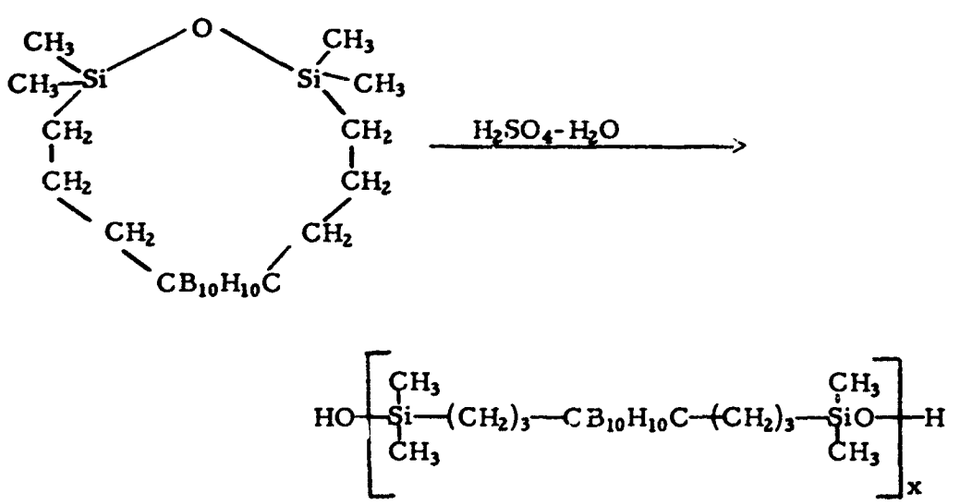
To prepare a copolymer with more siloxane units and hopefully greater elasticity, 1,7-bis(chlorodimethylsilylpropyl)-m-carborane and dichlorotetramethyldisiloxane were cohydrolyzed in 1:1 molar ratio (Equation 26). The product was a medium viscosity liquid of molecular weight 2500.



(26)

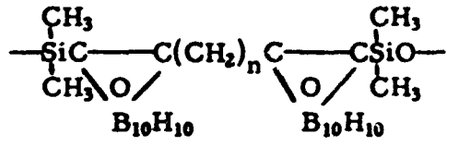
d. Ring-Opening Polymerization

The cyclic compound, 1-oxa-2,12-disila-2,2,11,11-tetramethyl-6,7,8-(1,7-m-carboranylene)cyclododecane, yielded polymer of molecular weight 8500 when treated with concentrated phosphoric acid and a similar product when treated with concentrated sulfuric acid (Equation 27). These products were

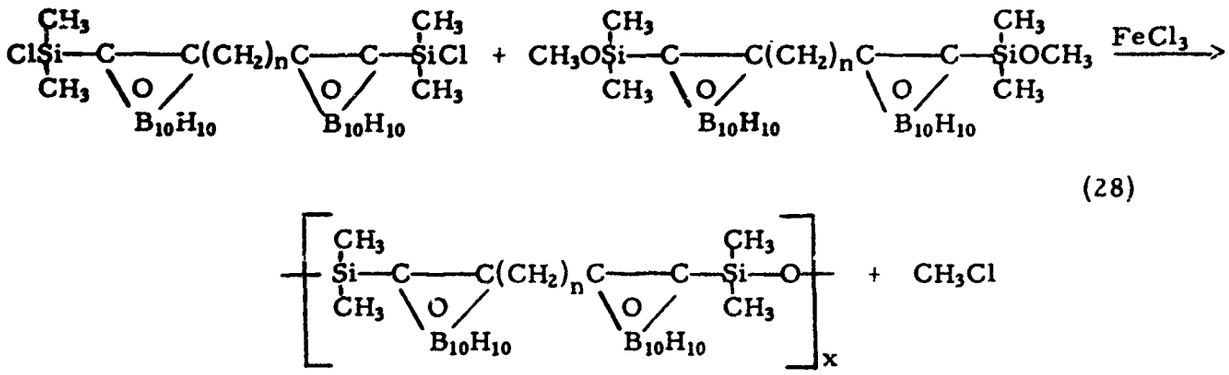


(27)

elastomeric gums and were completely soluble in aromatic solvents. Product of apparently higher molecular weight was obtained by use of diluted sulfuric acid catalyst. The effect of diluting the catalyst has been discussed by Andrianov (Ref 18). The higher polymer was a considerably tougher and more elastomeric gum; however, it was no longer soluble in aromatic solvents, and the molecular weight is not known.

2.  Structures

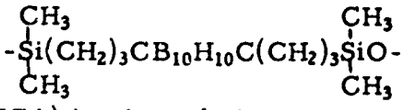
Polymers were prepared for which n=3 and 5 by alkoxysilane-halosilane condensation of chlorosilyl and methoxysilyl derivatives of dicarboranylpropyl and dicarboranylpentyl compounds respectively (Equation 28).



(28)

It was noted above that these compounds hydrolyze with cleavage at silicon-carborane bond, thus they could not be polymerized by hydrolysis-condensation. The alkoxide-halide condensation, catalyzed by ferric chloride, yielded polymers of up to 4000 molecular weight. The polymer, for which n=3, was a brittle solid of melting range 170-185°C. The n=5 polymer was a slightly elastomeric gum. The infrared spectrum of this polymer is shown in Figure 10.

D. Thermal Stability of Polymers

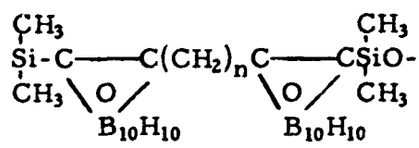
Thermal stability of polymer of structure  was determined by thermogravimetric analysis (TGA) in air and nitrogen atmospheres (Figure 11 and 12). Oxidative thermal degradation started at 240°C and continued with weight loss to 500°C. At this temperature a weight gain occurred which is probably due to oxidation of carborane to nonvolatile boron oxides. Nonoxidative degradation of the polymer started at about 370°C. Thus the weight loss that occurred between 240 and 370°C in air was due to oxidation. Since this amounted to 20% and was greater than weight loss that could result from oxidation of only methyl groups (<10%), it is apparent that oxidation occurred elsewhere. The most probable site of additional oxidation is at the Si-C bonds in the polymer backbone.

The thermal stability of this polymer was also evaluated by determination of molecular weight changes after heating at 300 and 350°C in nitrogen atmosphere. The results (tabulated below) indicated that no significant degradation occurred at these temperatures and supported the TGA data which indicated nonoxidative degradation starting at 370°C.

Thermal Degradation of Carborane Siloxane Polymers in Nitrogen

| Temperature °C | Time hr. | Molecular weight Original | After Heating |
|---|---|---|---|
| 300 | 24 | 6300 | 7800 |
| 350 | 24 | 6300 | 6000 |

Polymers of structures,

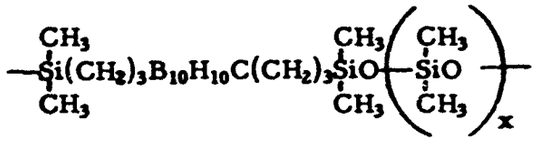


where n=3 and 5, were characterized for thermal stability by TGA and differential thermal analysis (DTA). The polymer, for which n=3, was stable in air and in nitrogen to 350°C (Figures 13 and 14). The TGA in air shows a drastic weight loss at about 410°C which is not apparent in nitrogen and is undoubtedly due to oxidative degradation. DTA's in air and nitrogen (Figures 15 and 16) show an exotherm, which is attributable to nonoxidative thermal degradation, starting at about 375°C. The DTA in air exhibits an additional sharp and large exotherm starting at 420°C which is due to oxidation. The small endotherms seen in both air and nitrogen at about 110° and 185°C apparently indicate transitions. The 110°C endotherm could be the second order transition or it could be the evaporation of adventitious moisture. The 185°C endotherm is undoubtedly a transition, probably the first order transition, since this is in the range of the observed polymer melting temperature. Following the first order transition there is a continuous gradual rise which, since it is not accompanied by any substantial weight loss as shown by the TGA's, may be due to additional polymerization in the molten state or instrument drifting.

TGA's of the polymer for which n=5 show decomposition in nitrogen and air beginning at about 250°C (Figures 17 and 18). Since the decomposition also occurs in nitrogen it is not oxidative decomposition. DTA's in nitrogen and air both show the nonoxidative decomposition as an exotherm beginning at about 250°C (Figure 19). In nitrogen, there is another exotherm beginning at about 440°C which may be due to thermal isomerization of o-carborane. The DTA in air shows an exotherm beginning at about 350°C, which is apparently an oxidative degradation. This exotherm, which shows an inflection at 420°C, is indicative of oxidation of pentane groups and silylmethyl groups. By comparison, the polymer for which n=3 showed the first oxidative exotherm starting at 420°C. This indicates oxidative stability of the propane groups to at least 420°C, and that the oxidation seen in the n=5 polymer at 350°C probably is due to the pentane groups.

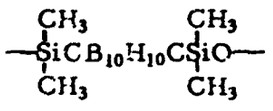
## III. DISCUSSION OF RESULTS

The objective of this program was the synthesis of thermally stable carborane siloxane elastomers. The initial approach toward this objective was the preparation of polymer structure I, where x = 0, 1, and 2.



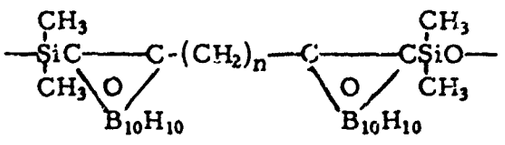
The polymers were obtained as gums of molecular weights 5000-8500 and higher. The higher polymers did not dissolve and molecular weights are not known, but these materials were tough elastomeric gums of apparently high molecular weight and demonstrated the flexibility of the polymer chain.

Examination of the polymer structure (x=0) for thermal and thermal oxidative stability showed stability in an inert atmosphere to 370°C (700°F) but decomposition in air at 240°C (465°F). These results indicated that carborane may have retarded the thermal rearrangements that polysiloxane chains normally undergo, but it did not inhibit oxidative attack on the silyl methyl groups. It has been determined in other work, however, that carborane does inhibit oxidative attack when the carborane is positioned adjacent to silicon as in structure II (Ref 2 ).



II

With the objective of obtaining a polymer that was both flexible and thermally stable, polymers of structure III where n = 3 and 5 were prepared.



III

It was anticipated that, in these structures, carborane would stabilize the silyl-methyl groups as well as the polymethylene chain toward thermal oxidation and that the polymethylene chain would give flexibility to the polymer molecule. It was shown that the carborane did stabilize the methyl groups and apparently

the trimethylene chain; however, the trimethylene chain did not give the polymer sufficient flexibility. A pentamethylene chain gave the polymer additional flexibility and the material had marginal elastomeric properties, but the pentamethylene grouping was not thermally stable.

The problem was resolved into a search for a linking group for the carboranes that would be both thermally stable and flexible. It was toward this end that the attempt was made to prepare a dicarboranylperfluoroalkane intermediate. This material would have allowed the preparation of polymer with fluorocarbon linking groups that may be more stable than the hydrocarbon derivatives; however, this work was not completed before the end of the program.

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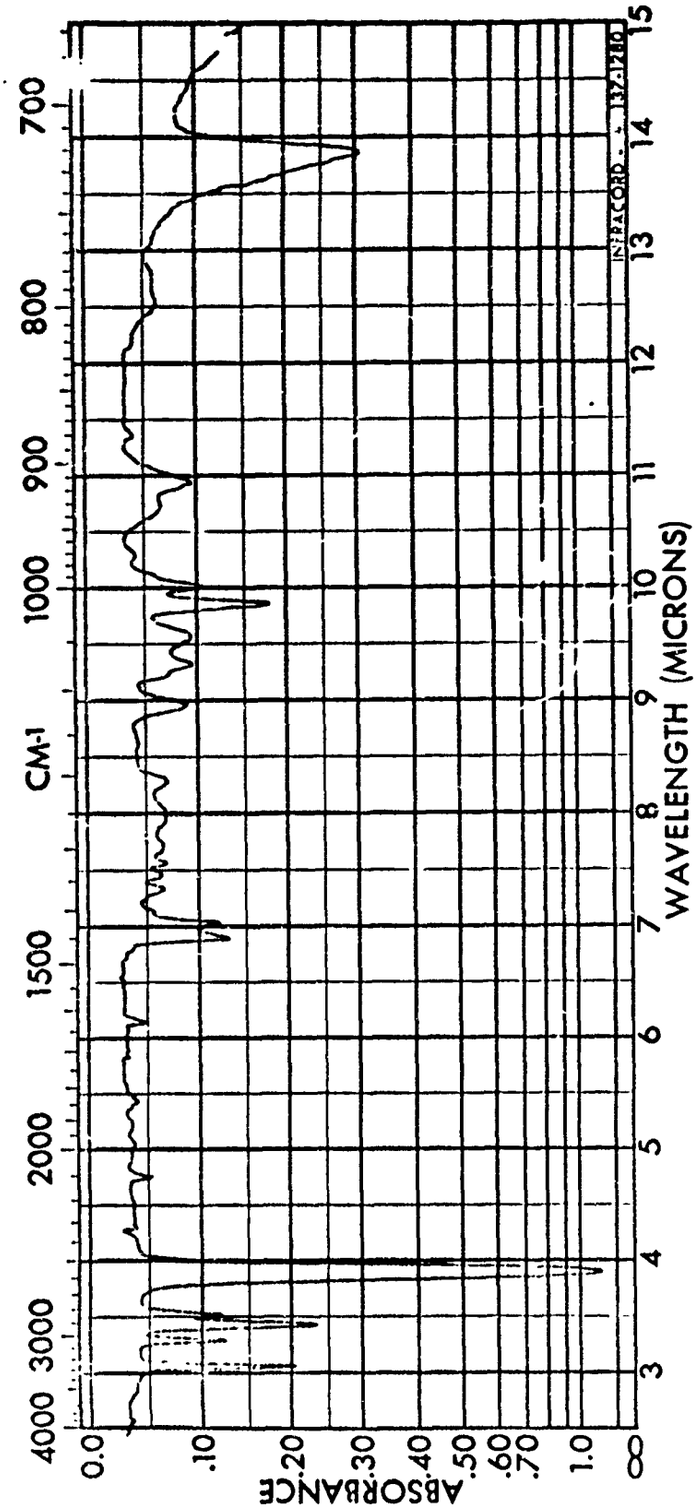


Figure 1. Infrared Spectrum of 6-o-Carboranylhex-1-yne

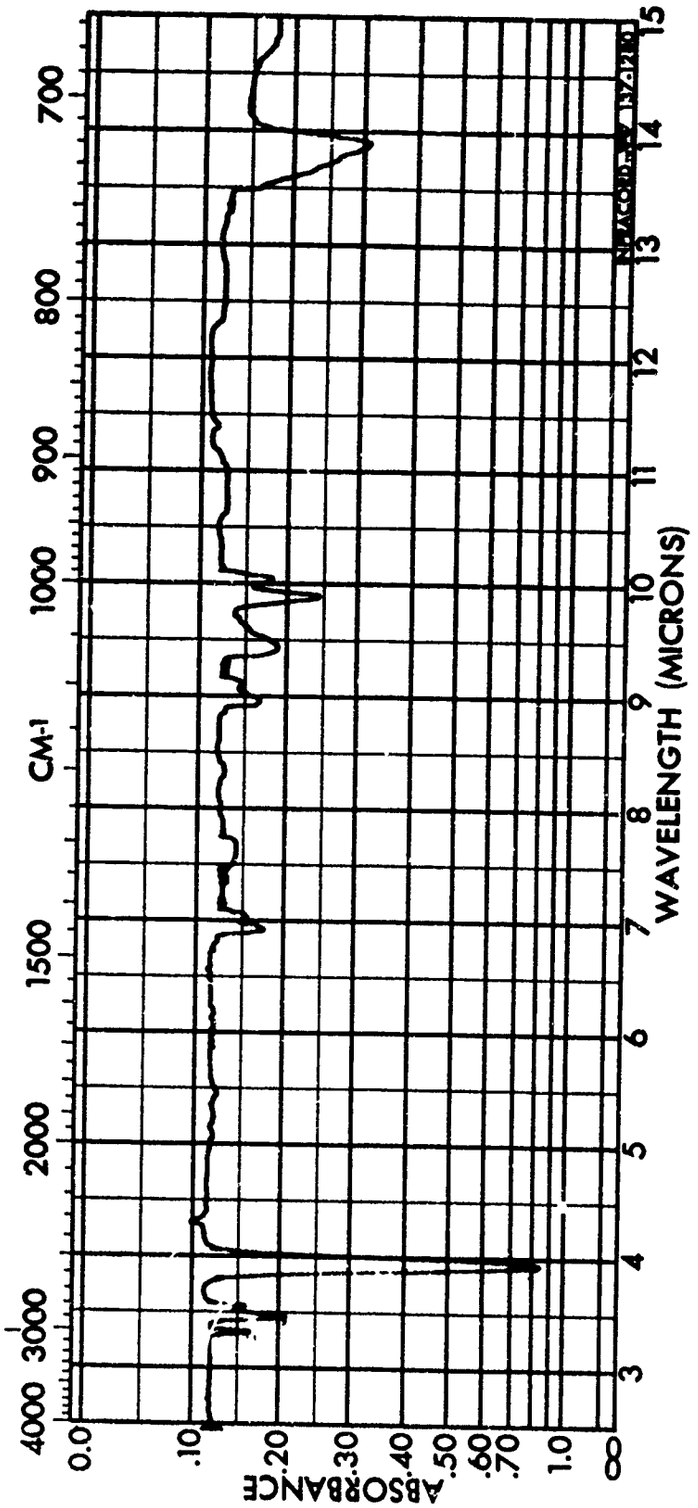


Figure 2. Infrared Spectrum of 1,5-Di-o-carboranylpentane

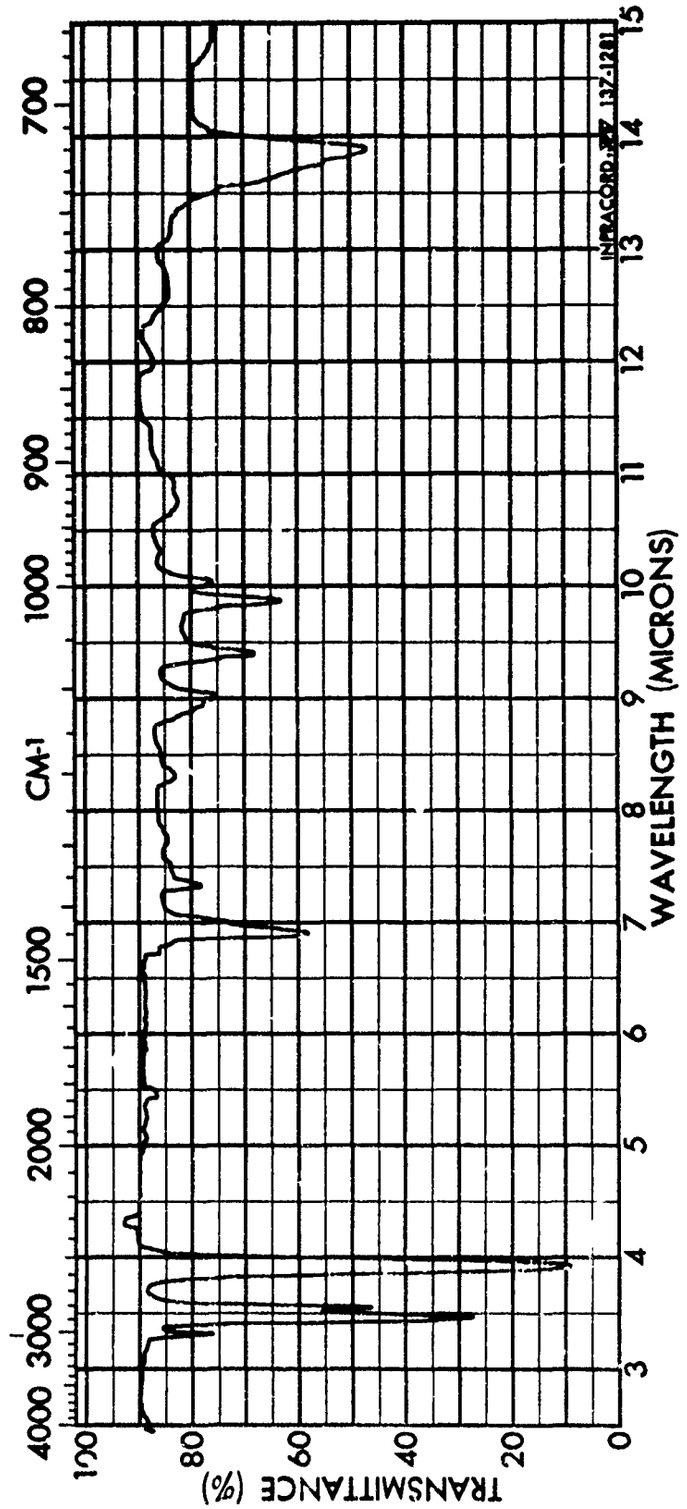


Figure 3. Infrared Spectrum of "n-Heptylcarborane"

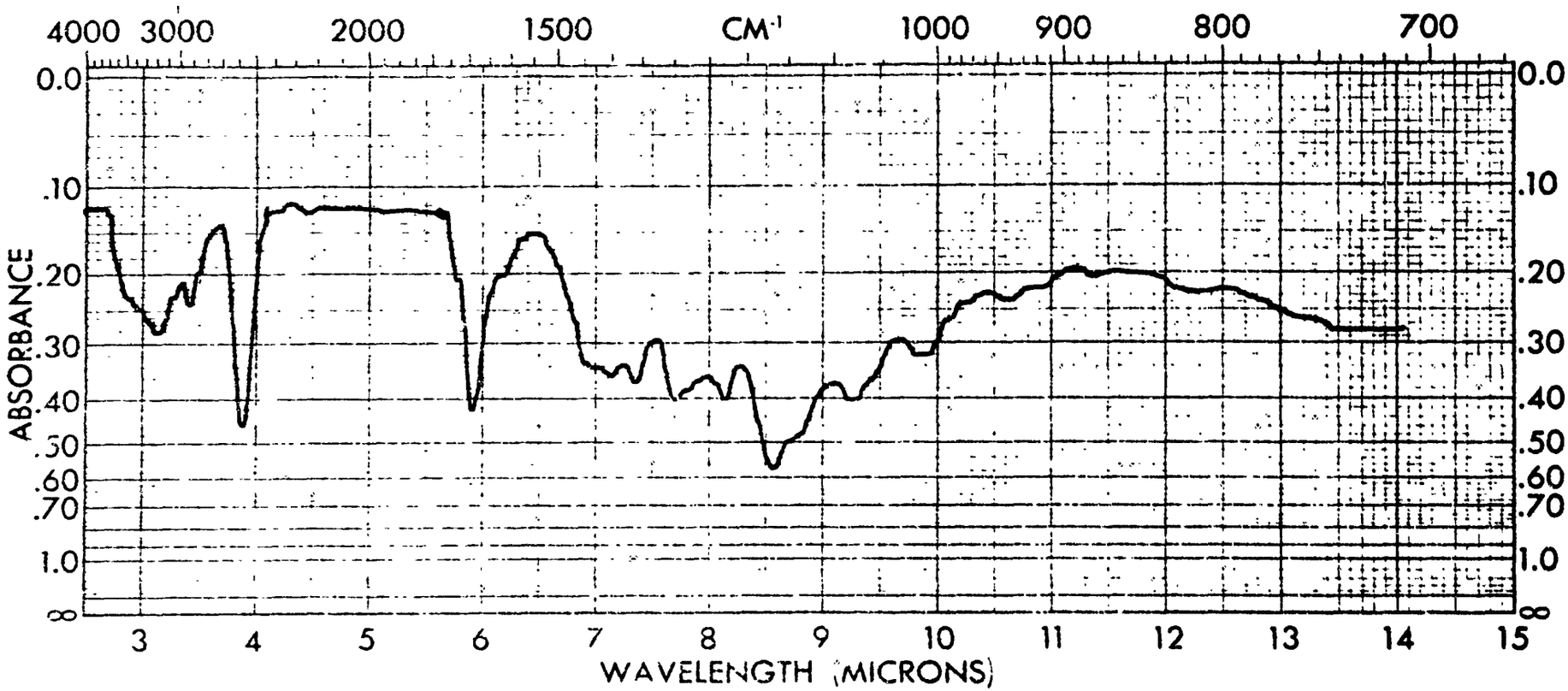


Figure 4. Infrared Spectrum of the Ether Insoluble Product of the Lithio-m-carborane/ Perfluoroglutaryl Chloride Reaction

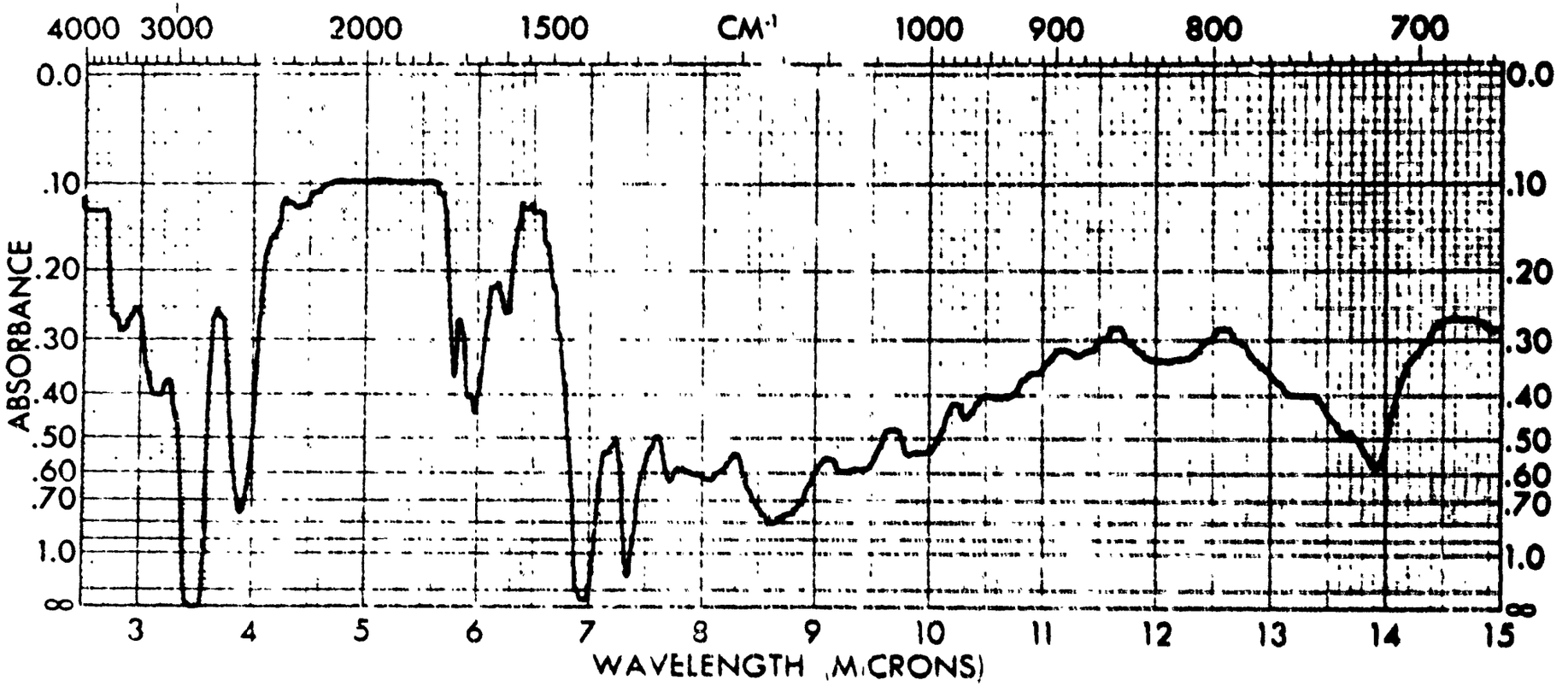


Figure 5. Infrared Spectrum of the Ether Soluble Product of the Lithio-m-carborane/ Perfluoroglutaryl Chloride Reaction (Nujol Mull)

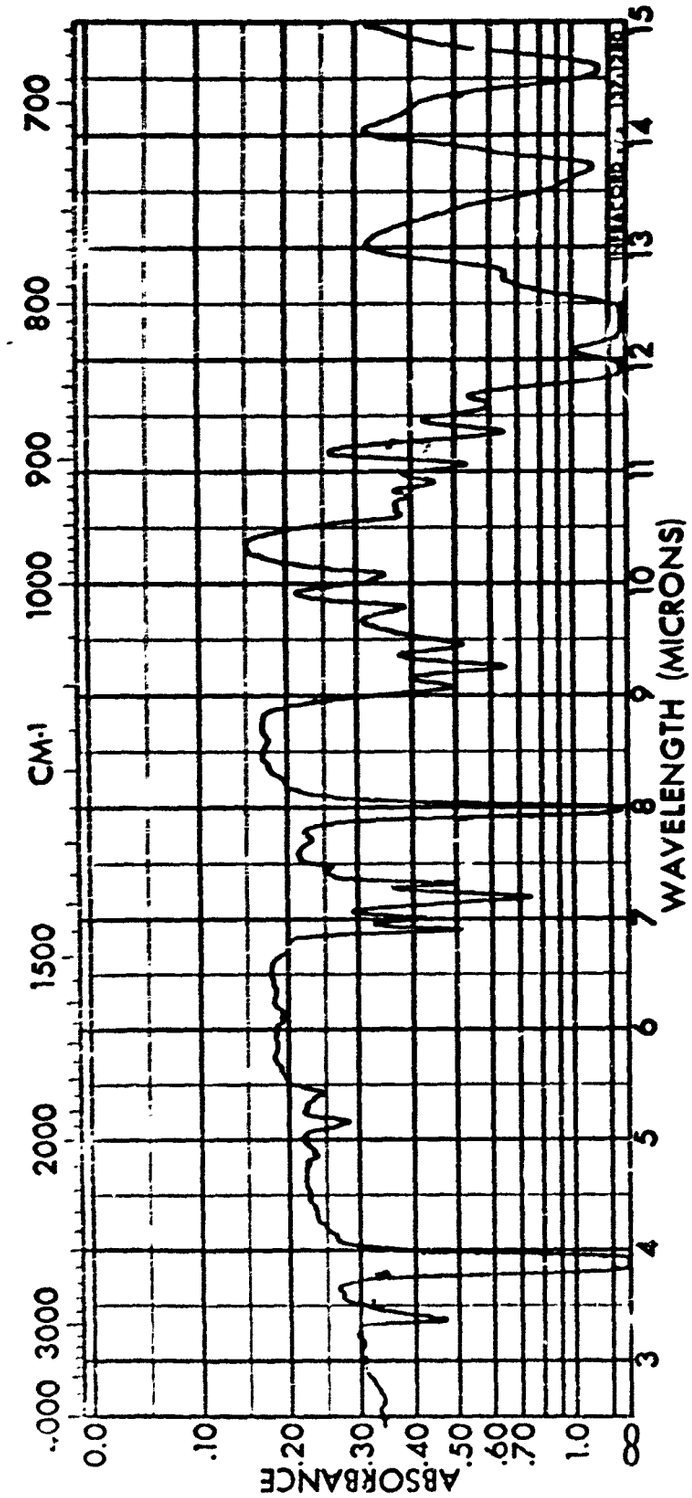


Figure 6. Infrared Spectrum of Bis(1-chlorodimethylsilyl-o-carboran-2-yl) propane

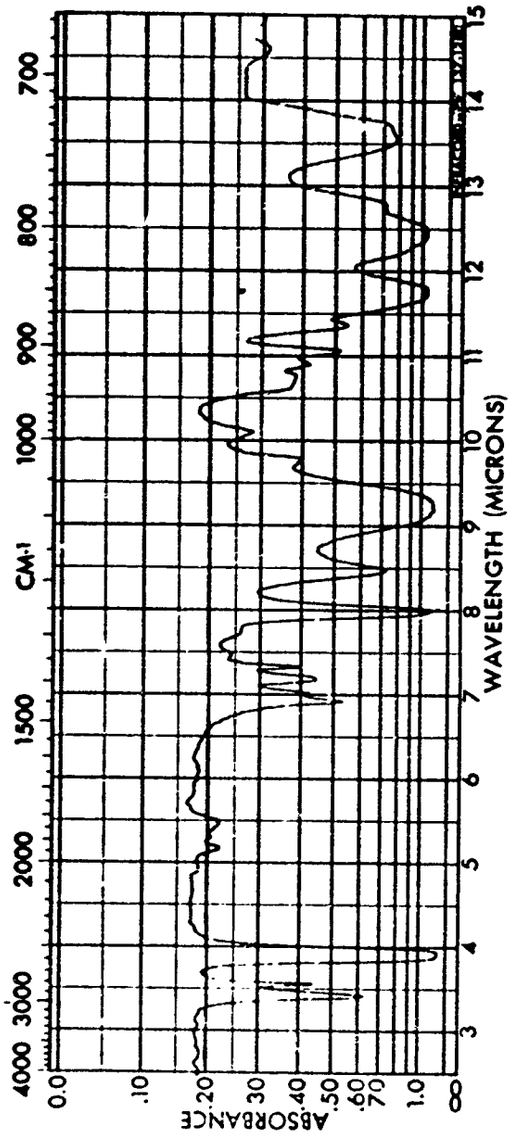


Figure 7. Infrared Spectrum of Bis(1-methoxydimethylsilyl-o-carboran-2-yl)-propane

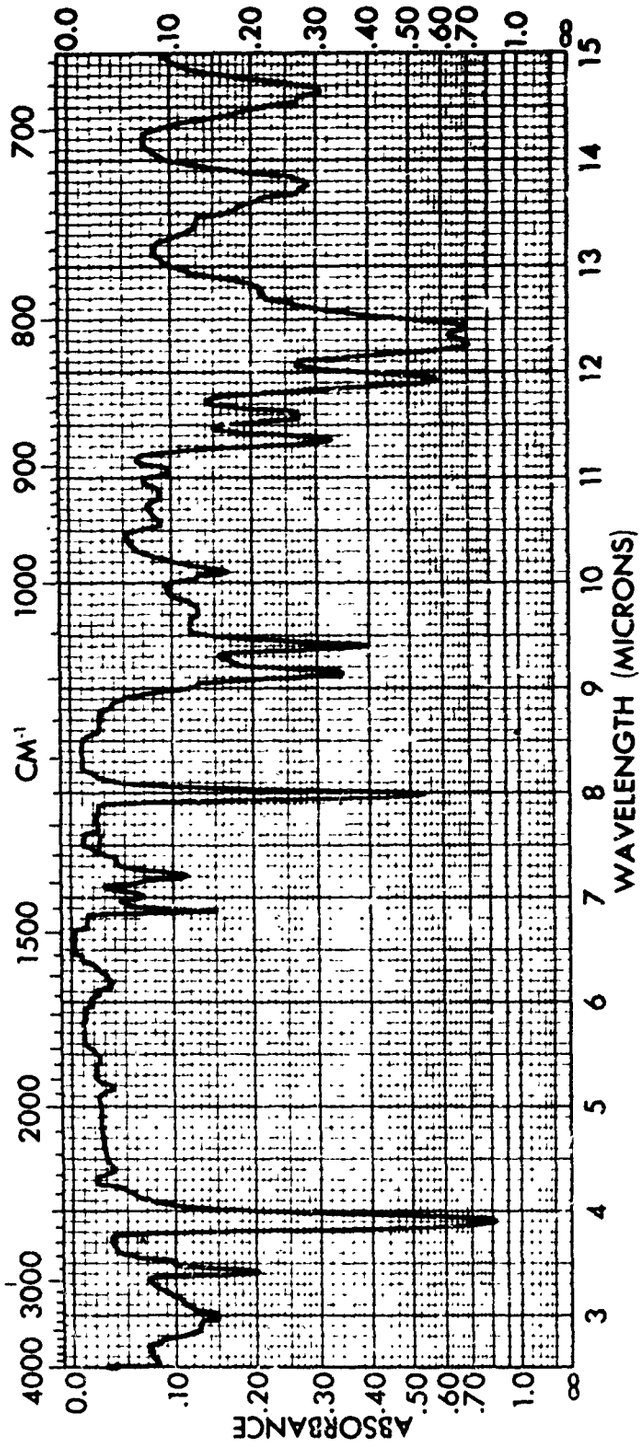


Figure 8. Infrared Spectrum of 1,5-Bis(1-chlorodimethylsilyl-o-carboran-2-yl)pentane

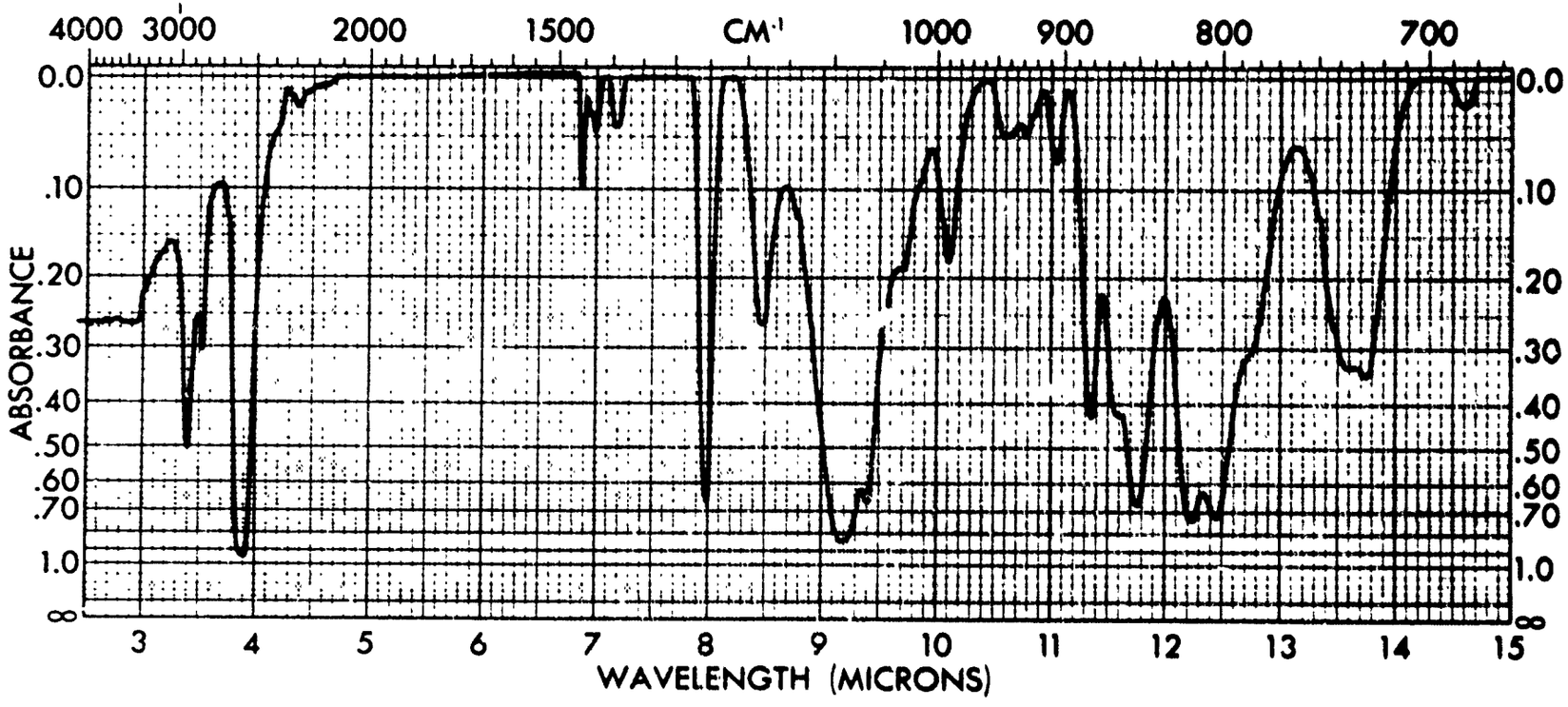


Figure 9. Infrared Spectrum of 1,5-Bis(1-methoxydimethylsilyl-o-carboran-2-yl)pentane



Thiokol

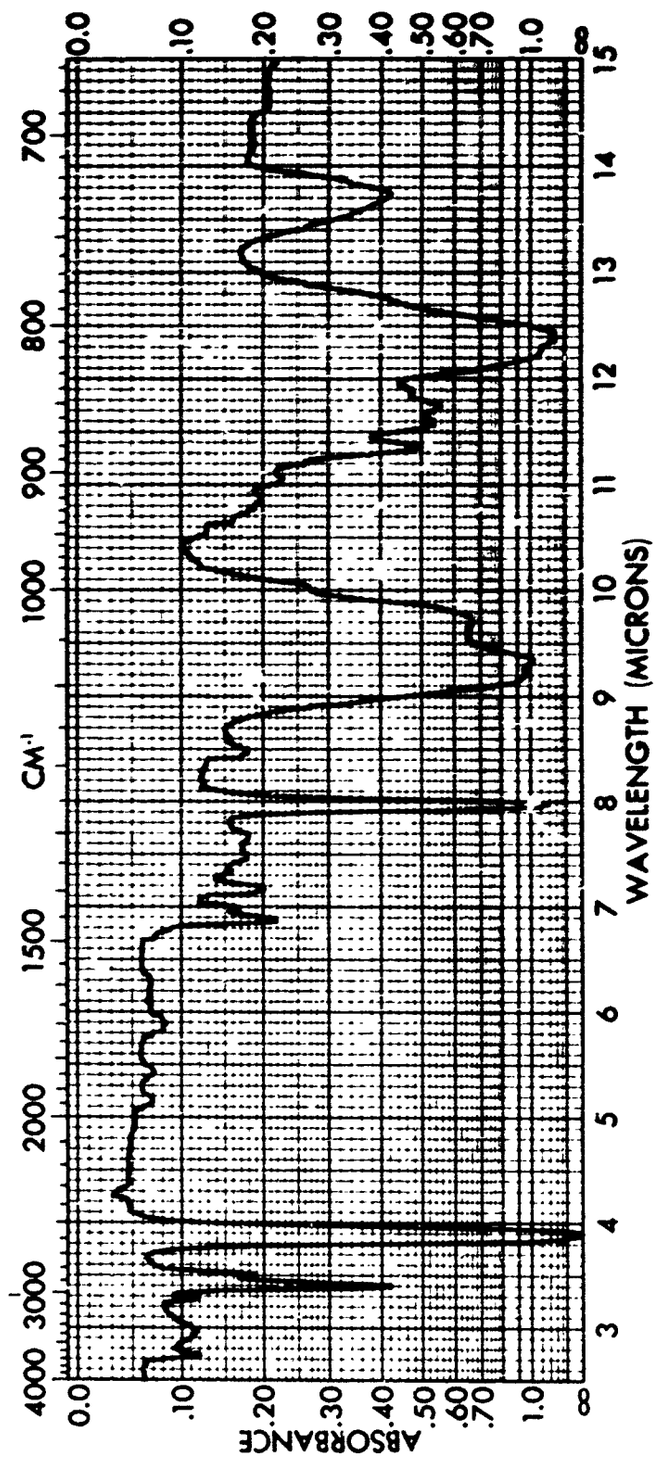


Figure 10. Infrared Spectrum of Dicarboranylpentane Polysiloxane

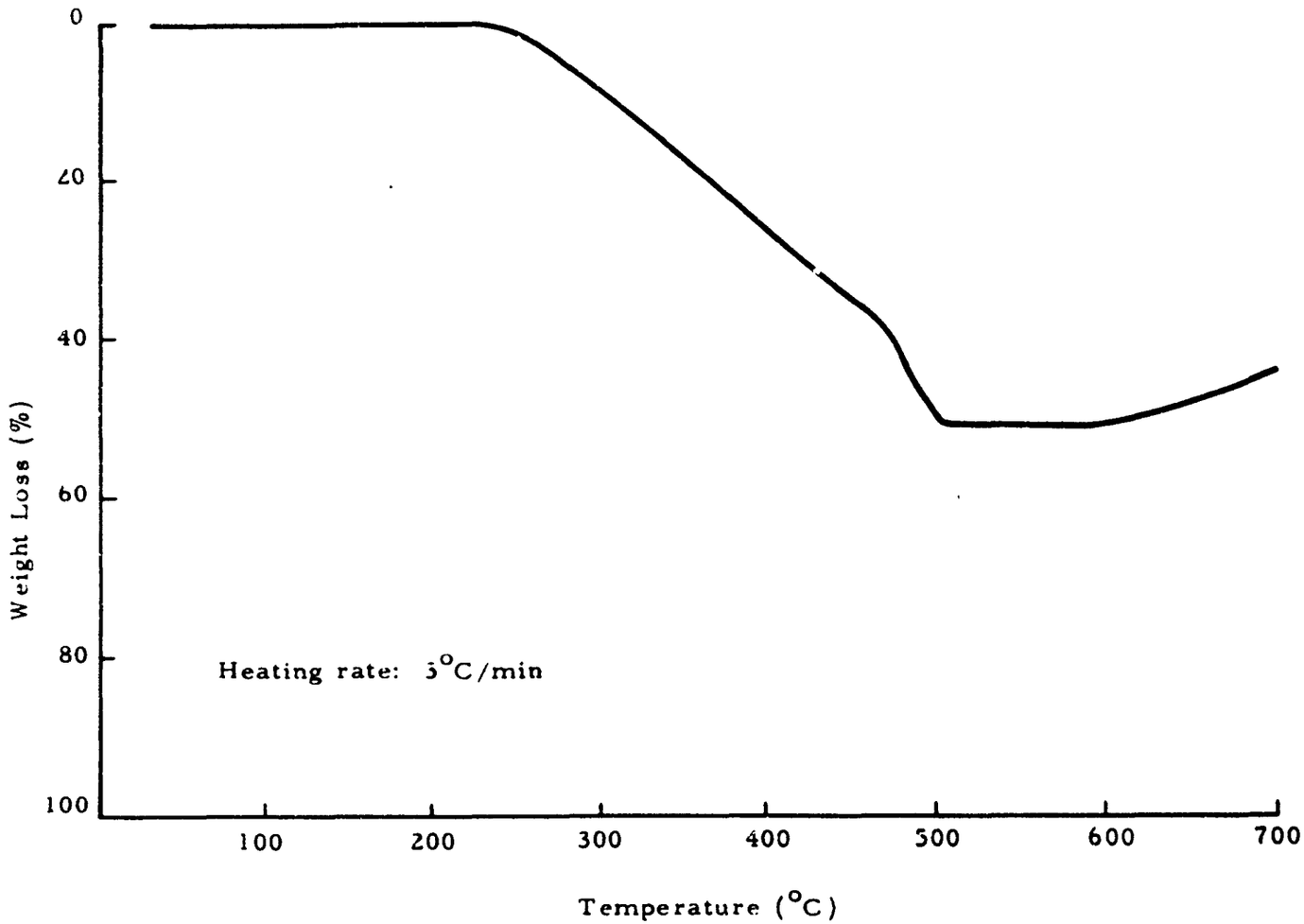


Figure 11. TGA of $\left[ O\,\overset{CH_3}{\underset{CH_3}{Si}}\,(CH_2)_3\,CB_{10}H_{10}C\,(CH_2)_3\,\overset{CH_3}{\underset{CH_3}{Si}} \right]_x$ in Air



Thiokol
REACTION MOTORS DIVISION

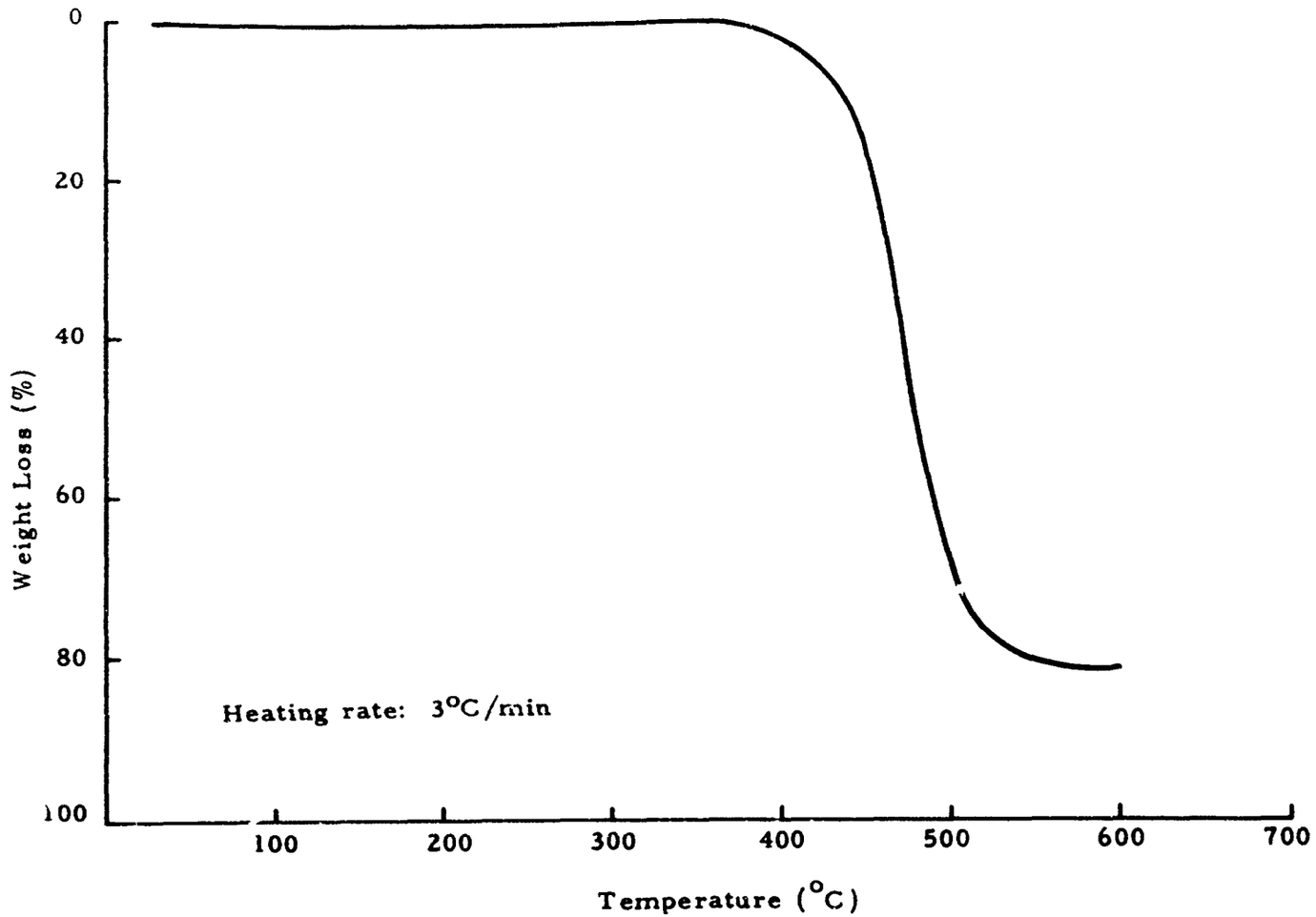


Figure 12. TGA of $\left[ O\,\overset{CH_3}{\underset{CH_3}{Si}}\,(CH_2)_3\,CB_{10}H_{10}C\,(CH_2)_3\,\overset{CH_3}{\underset{CH_3}{Si}} \right]_x$ in $N_2$



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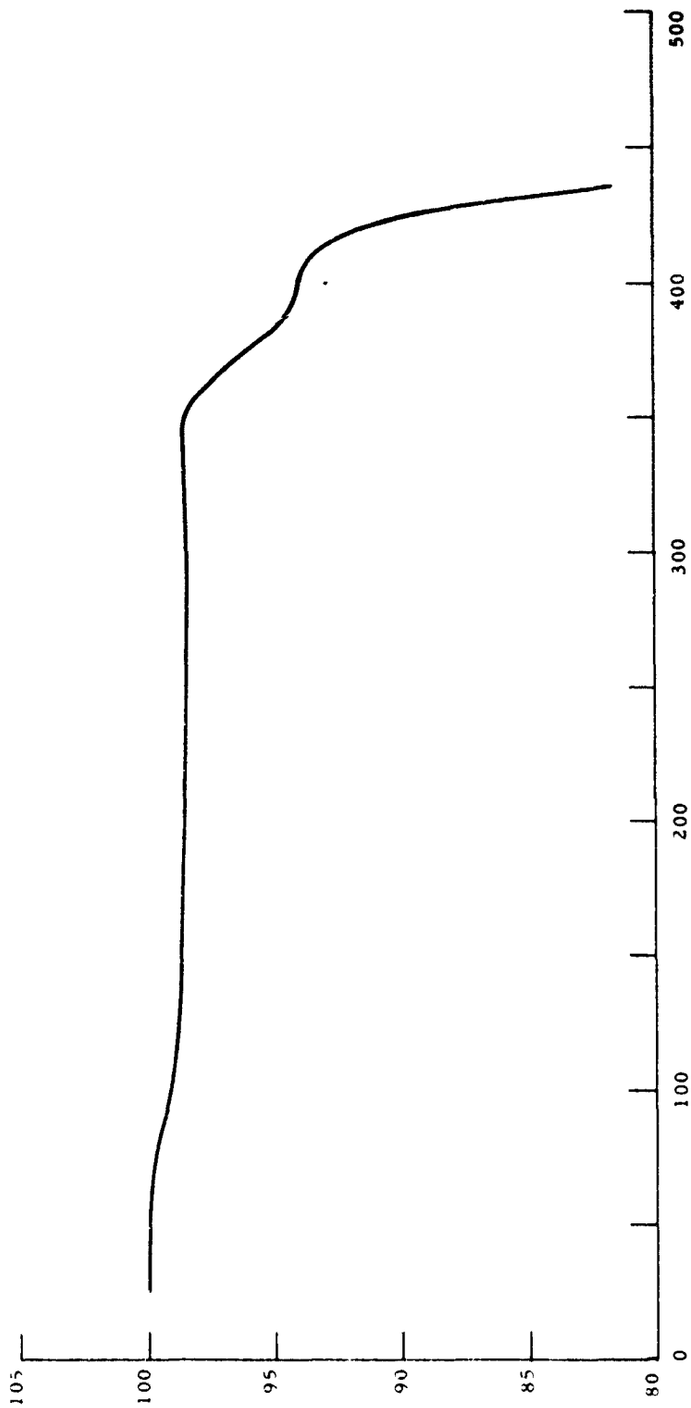



Figure 13. TGA of Dicarboranylpropane Polysiloxane

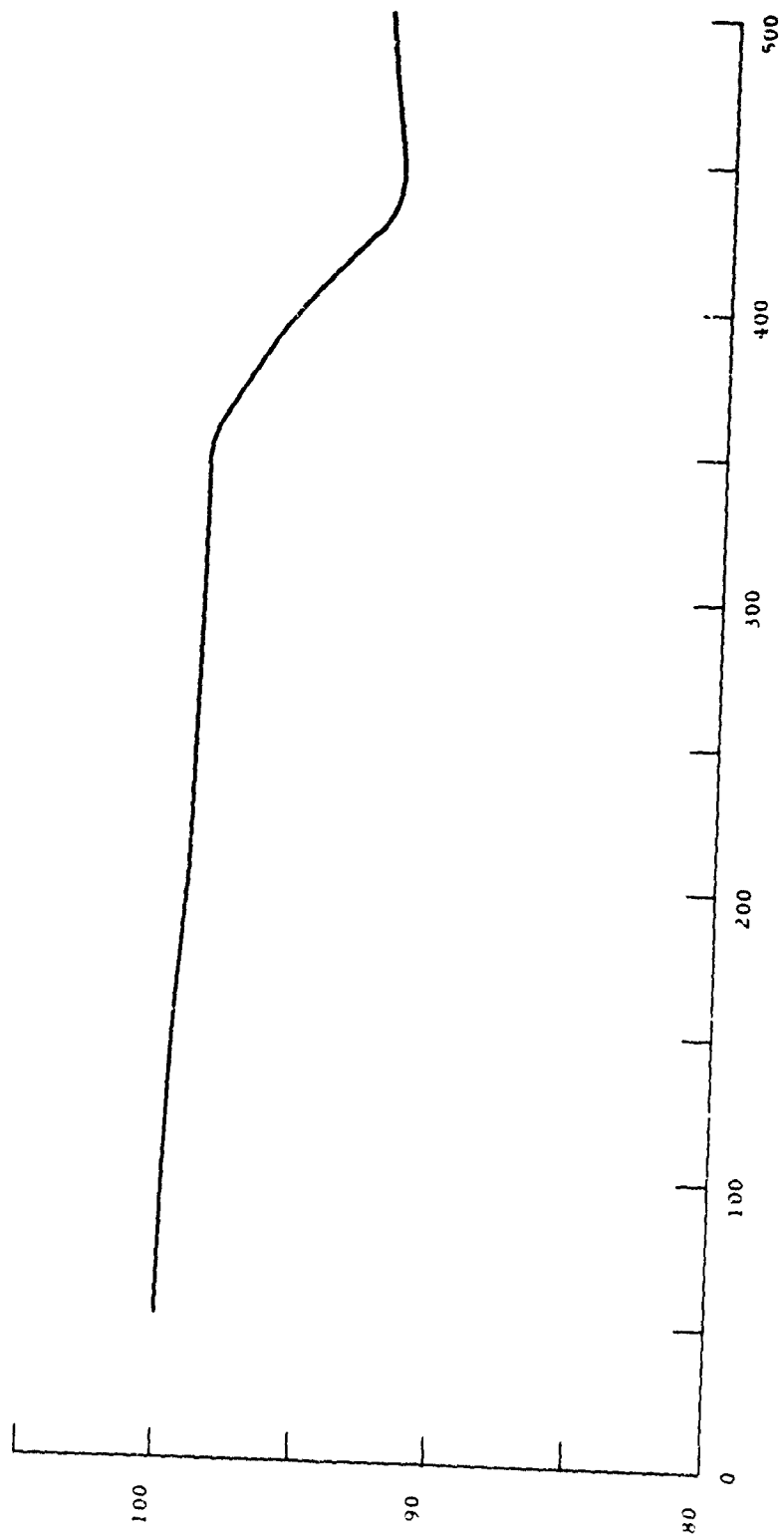



Figure 14. TGA of Dicarboranylpropane Polysiloxane in Nitrogen

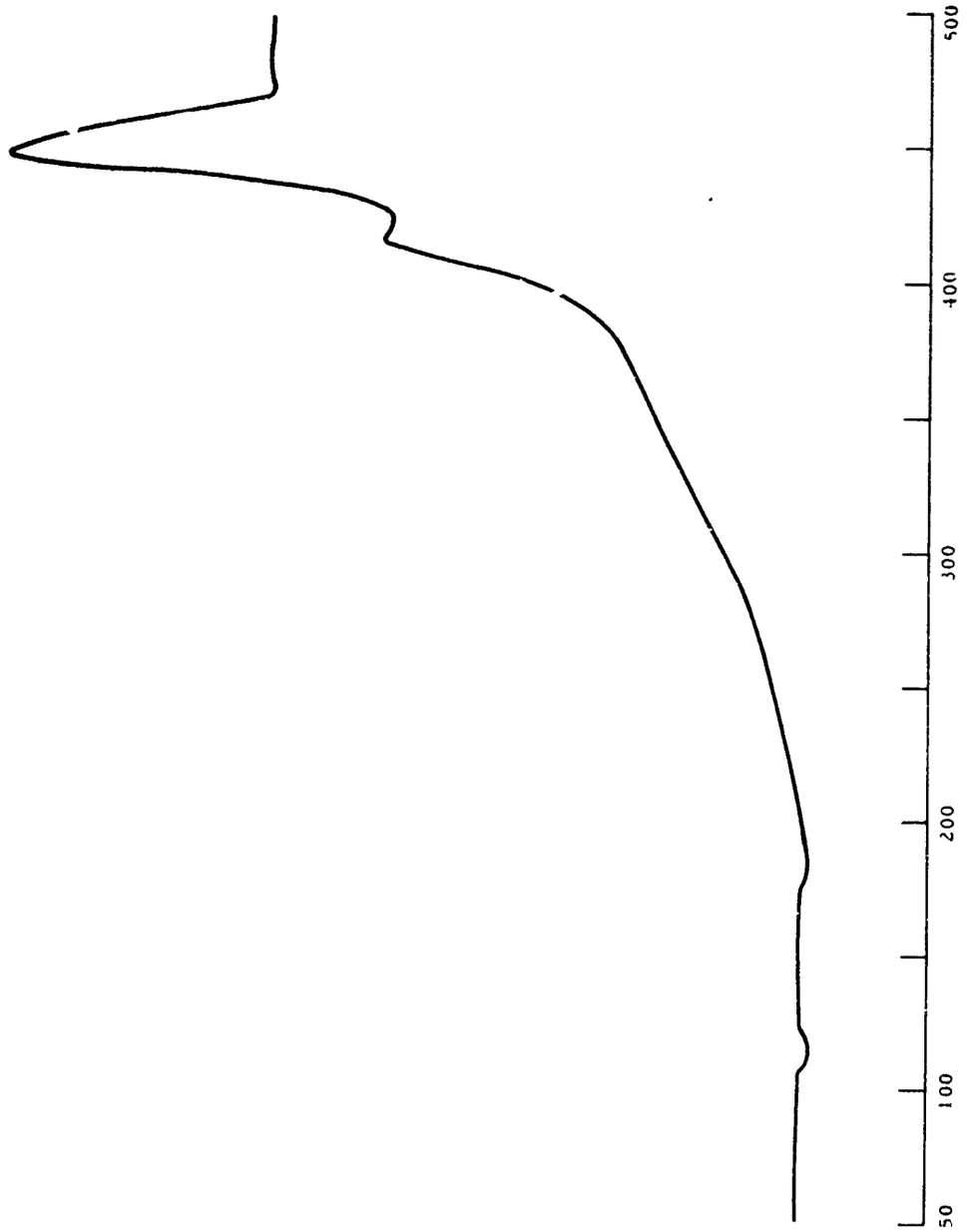



Figure 15. DTA of Dicarboranylpropane Polysiloxane in Air

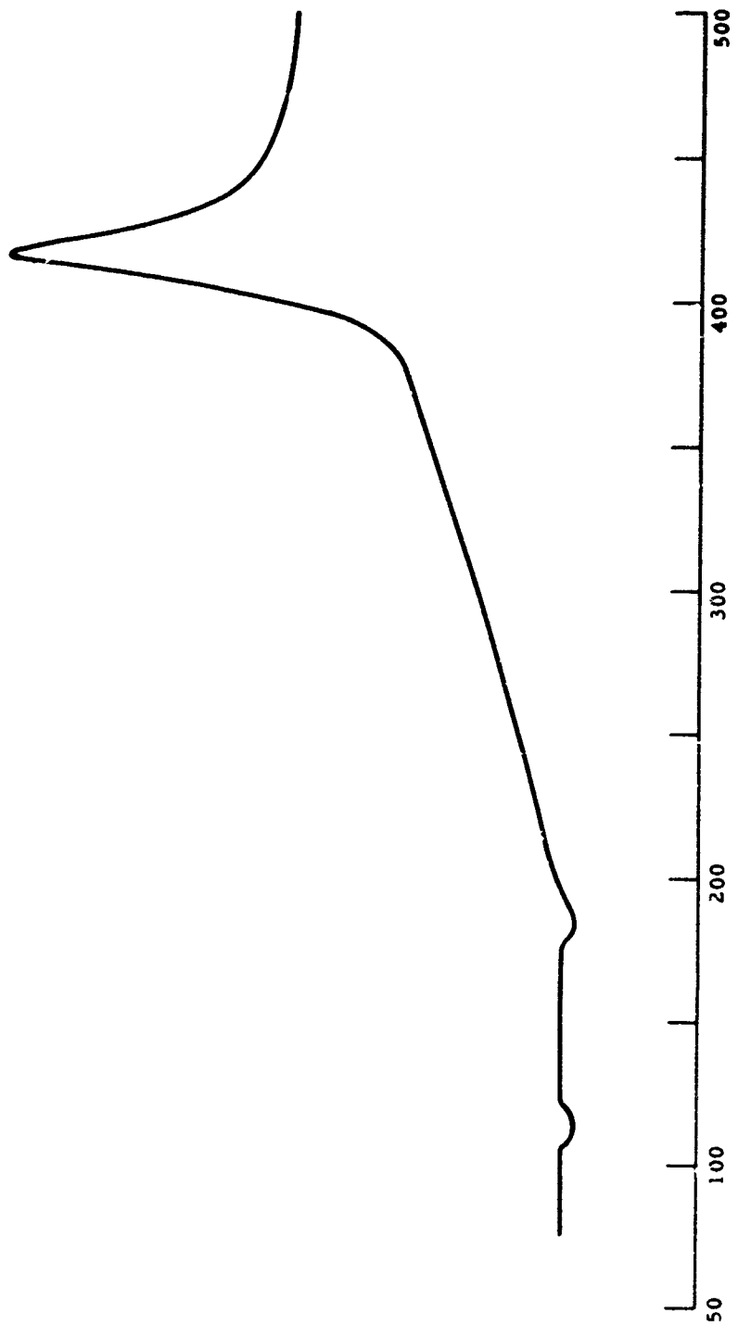



Figure 16. DTA of Dicarboranylpropane Polysiloxane in Nitrogen

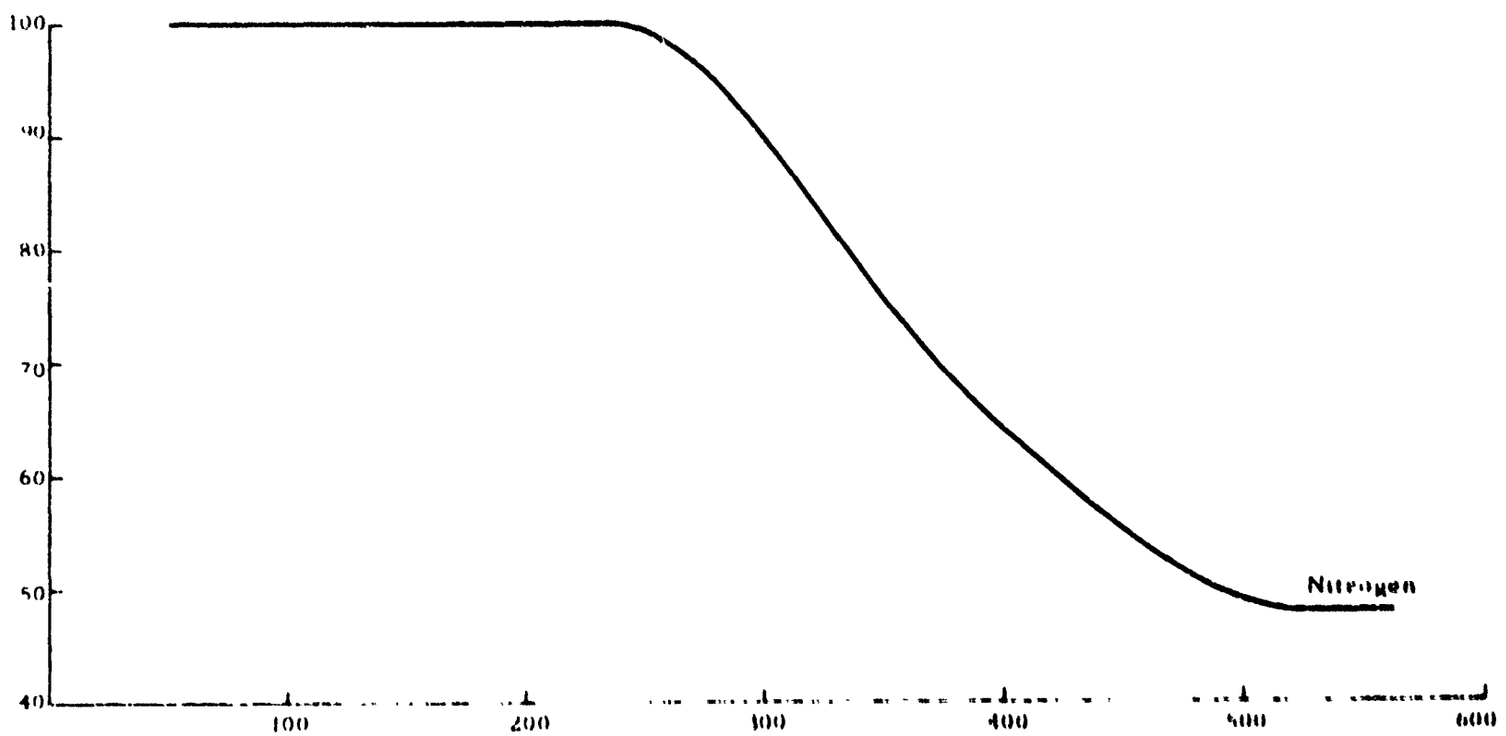



Figure 17. TGA of Dicarboranylpentane Polyarloxane in Nitrogen



Thiokol

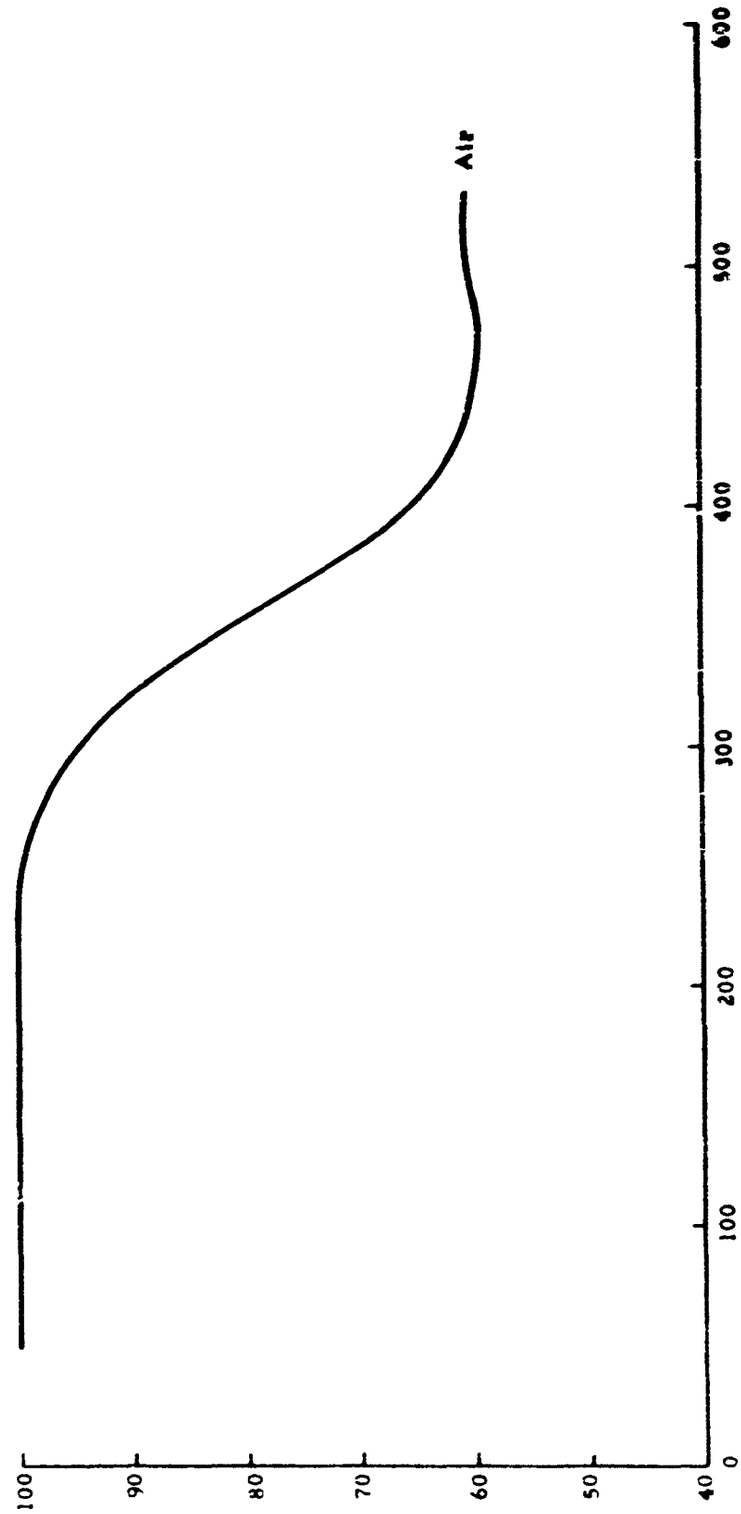



Figure 18. TGA of Dicarboranylpentane Polysiloxane in Air

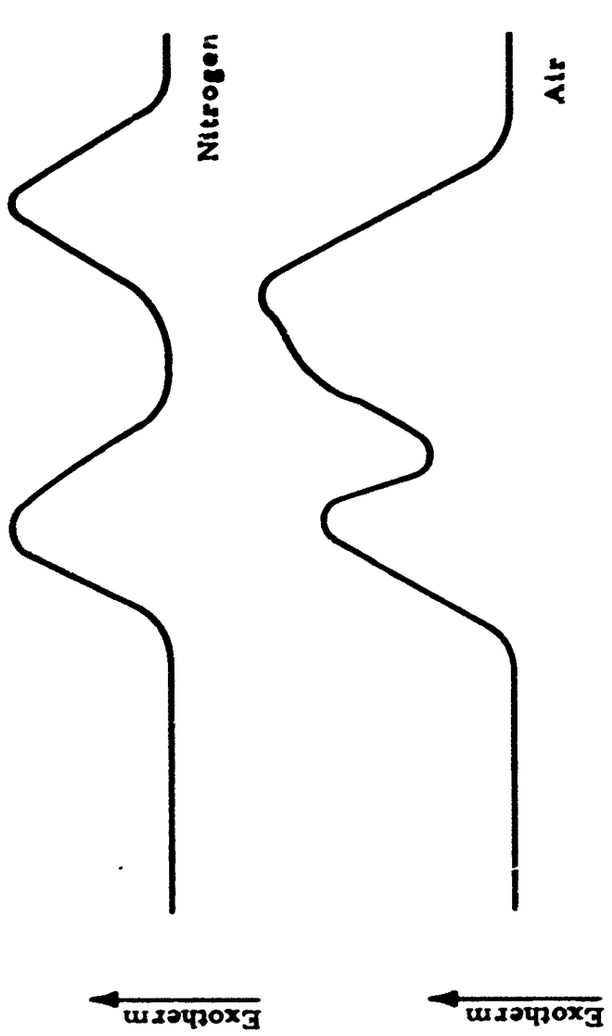
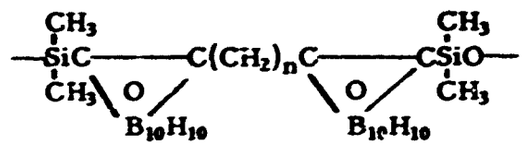



Figure 19. DTA of Dicarboranylpentane Polysiloxane in Air and Nitrogen

## ABSTRACT (cont'd)



where n= 3 and 5

II

Polymers of structure I. of molecular weight 8,500 and higher, were elastomeric. Thermal stability evaluation by TGA and DTA indicated oxidative degradation at 240°C, no significant improvement over noncarborane polysiloxanes.

Polymer of structure II, where n=3, was nonelastomeric (mp 170-185°C), but TGA and DTA indicated this polymer to be stable to 350°C and oxidatively stable to 410°C. A polymer of similar structure, where n=5, had improved physical properties (slightly elastomeric gum) but lower thermal stability. Thermal analysis of this polymer indicated a nonoxidative decomposition at 250°C and an oxidative decomposition at 350°C.

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3. REPORT TITLE

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4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Final Report - 19 February 1965 through 18 February 1967

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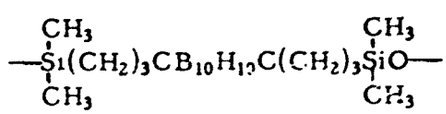
13. ABSTRACT


Toward the objective of synthesizing thermally stable elastomeric carborane-siloxane polymers, silane, carborane, and silane-carborane intermediates and monomers were prepared. Chlorosilanes, alkoxysilanes and a cyclic siloxane monomer were polymerized by heterogroup condensation, hydrolysis-condensation and ring-opening polymerization techniques. Polymers were obtained that ranged from viscous liquids and brittle solids to elastomeric gums depending on polymer molecular weight and structure.

Two types of polymer structures (I and II) were synthesized.



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| 14 KEY WORDS | LINK A ROLE | LINK A WT | LINK B ROLE | LINK B WT | LINK C ROLE | LINK C WT |
|---|---|---|---|---|---|---|
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| Carborane Monomers | | | | | | |
| Carborane Polymers | | | | | | |
| Polysiloxanes | | | | | | |
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