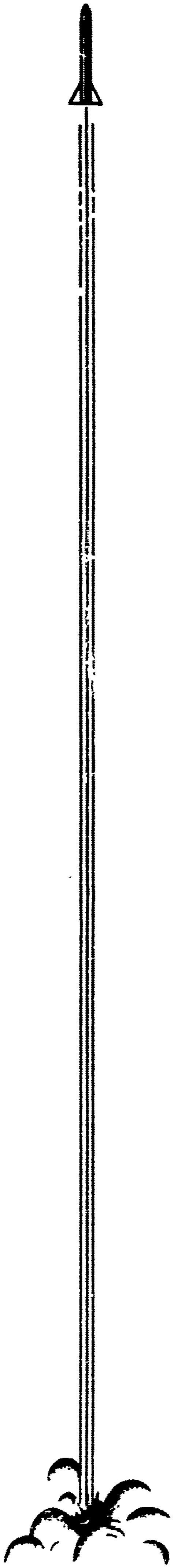

Report RMD 5065-Q5
Contract No. DA-11-070-AMC-852 (W)

# CARBORANE - SILOXANE ELASTOMERS

Report Period: 19 February 1966 through 18 May 1966

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Thiokol
CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVILLE, NEW JERSEY

Thiokol
REACTION MOTORS DIVISION

# CARBORANE SILOXANE ELASTOMERS

RMD Report 5065-Q5

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

Report Period: 19 February through 18 May 1966

Submitted by: Joseph Green
JOSEPH GREEN, Supervisor
Applied Chemical Research
Section

Approved by:
MURRAY S. COHEN
Manager
Chemistry Department

David J. Mann
DAVID J. MANN
Director of Research

# 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 covers work done in the fifth quarter of the program during the period 19 February through 18 May 1966. Mr. Z. T. Ossefort of Rock Island Arsenal is the Project Engineer. Contributors at Thiokol are: Mr. Nathan Mayes (Principal Scientist) and Mr. Alan Jackson. The program is under the general direction of Dr. M. S. Cohen and Mr. Joseph Green.

## ABSTRACT

The carborane silane monomers, bis(1-chlorodimethylsilyl-o-carboran-2-yl) propane and bis(1-methoxydimethylsilyl-o-carboran-2-yl)propane, were synthesized and copolymerized to a carborane polysiloxane. Thermal characterization of the polymer by TGA and DTA in air and nitrogen indicated thermal stability to 350°C with no oxidation evident until over 400°C. The thermal data illustrate the "protective action" of carborane and its ability to stabilize neighboring groups to thermal oxidative degradation.

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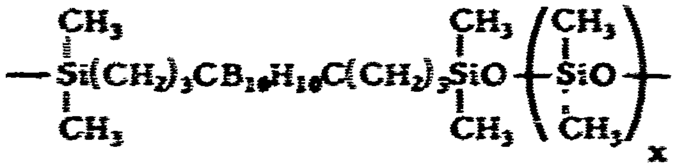
# I. INTRODUCTION

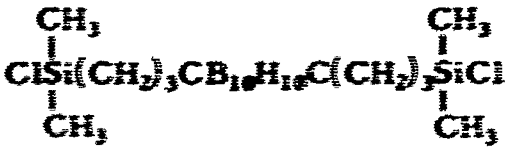
The objective of this program is the synthesis of thermally stable carborane siloxane elastomers. The initial approach toward this objective was the preparation of polymer structure I*, where x = 0, 1, and 2.



$$-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{(CH_2)_3CB_{10}H_{10}C(CH_2)_3}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{O}\left(-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{O}-\right)_x$$

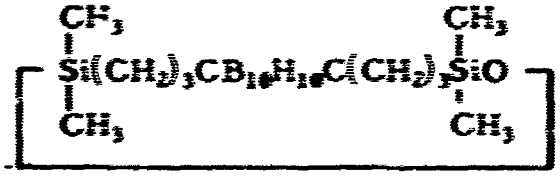
I

During the first two quarters of the program, this approach led to the preparation of several precursors and monomers including



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

and



$$\left[\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{(CH_2)_3CB_{10}H_{10}C(CH_2)_3}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{O}\right]$$

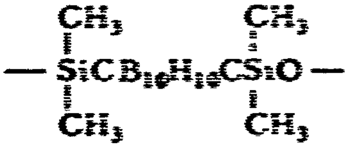
both of which were polymerized to polymers of the desired structures. The polymers were obtained as gums of molecular weights 5000-8500 and higher. The higher polymers did not dissolve and molecular weights are not known, but these materials were tough elastomeric gums of apparently high molecular weight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

---

* $\mathrm{-CB_{10}H_{10}C-}$ denotes 1, 7-dicarbaclovododecaborane commonly called m-carborane

Evaluation of polymer structure I (x= 0) for thermal and thermal-oxidative stability indicated stability in an inert atmosphere to 370°C (700°F) but decomposition in air at 240°C (465°F). These results indicated that carborane acted to retard the thermal rearrangements that polysiloxane chains ordinarily undergo, but it did not appreciably inhibit oxidative attack on the silyl methyl groups. With this knowledge, it became necessary to reexamine the approach that had been taken and to consider altering the course of the program.

The reason for the lack of thermal-oxidative stability in the polymer under discussion became apparent upon examination of some recently published work concerning carborane siloxane polymers of somewhat different structure (Ref 1). These polymers, with structures II, III, IV, and V, contained carborane adjacent to silicon.

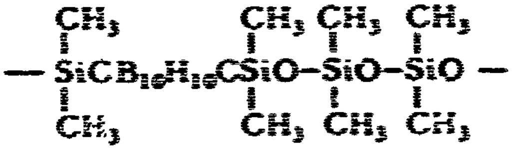


$$-\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\mathrm{CB_{10}H_{10}C}\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\mathrm{O}-$$

II

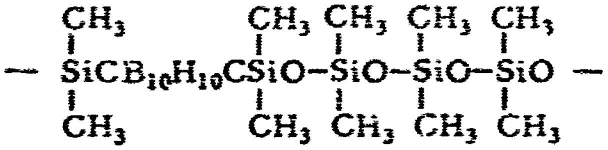
$$-\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\mathrm{CB_{10}H_{10}C}\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\mathrm{O}-\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\mathrm{O}-$$

III



$$-\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\mathrm{CB_{10}H_{10}C}\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\mathrm{O}-\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\mathrm{O}-\underset{CH_3}{\overset{CH_3}{\mathrm{Si}}}\mathrm{O}-$$

IV

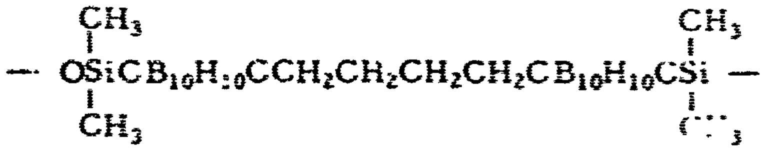


$$-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{CB_{10}H_{10}C}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{O}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{O}-$$

V

The polymer of structure II, with carborane adjacent to every silicon, exhibited stability to 500°C in an inert atmosphere and to 450°C in air. The polymers of structures III, IV, and V exhibited progressively lower thermal oxidative stabilities. The data indicated that carborane stabilizes adjacent silyl methyl groups and protects them from oxidative attack. Silyl methyl groups farther removed from carborane, as in polymers III, IV, and V, were not protected, and lower thermal-oxidative stabilities were observed for these polymers. Thus, it was apparent that polymers of structure I were not stable to thermal-oxidative attack because in these structures the carborane group is too far from the silyl methyl groups to protect them.

It is evident then that to obtain carborane siloxane polymers of high thermal-oxidative stability, the carborane must be positioned adjacent to silicon as in structure II. Structure II, however, is a high melting resin (mp 200°C) and to obtain elasticity, it is necessary to incorporate flexible linking groups into the polymer chain. The linking groups may not be dimethylsiloxanes as in III, IV, and V because the methyl groups are not stabilized by carborane and are susceptible to oxidation. The linking groups then must also be adjacent to carborane and in order to be within the known protective sphere of the carborane, the linking groups should contain no carbon atom that is more than one atom removed from carborane. Structure VI meets all of these requirements.



$$-\mathrm{O}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}\mathrm{CB_{10}H_{10}CCH_2CH_2CH_2CH_2CB_{10}H_{10}C}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{Si}}}-$$

VI

The third and fourth quarters of the program were devoted primarily to the synthesis of precursors and monomers toward the eventual preparation of structure VI or related structures. A dichlorosilane monomer that could lead to such structures was synthesized; however, it was not directly polymerizable and it has been necessary to prepare a dialkoxysilane monomer in order to effect polymerization.

## II. TECHNICAL PROGRESS

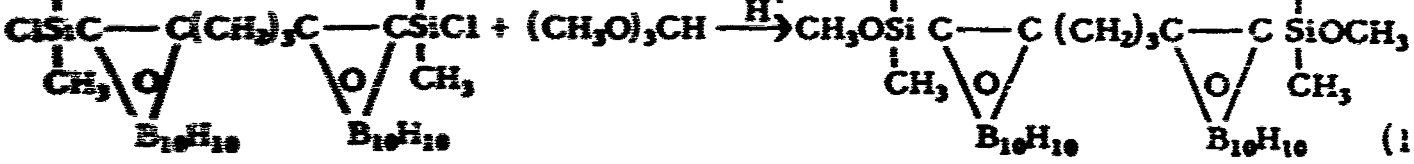
### A. MONOMER SYNTHESIS

### 1. Bis(1-chlorodimethylsilyl-*o*-carboran-2-yl)propane

The original synthesis of bis(1-chlorodimethylsilyl-*o*-carboran-2-yl)-propane was reported in the previous quarterly report (Ref 2). The synthesis has been repeated on a larger scale and a higher yield of the product has been obtained. Specifically, 32.8 gm of product (72% yield) was obtained from 30.2 gm (0.092 mole) of 1,3-di-*o*-carboranylpropane, treated with 0.184 mole of *n*-butyllithium and 1.84 moles of dichlorodimethylsilane. The product crystallized from the reaction mixture to crystals of mp 210-211°C. The product has been identified by infrared spectroscopy. Positive identification awaits a complete elemental analysis.

### 2. Bis(1-methoxydimethylsilyl-*o*-carboran-2-yl)propane

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



(1)

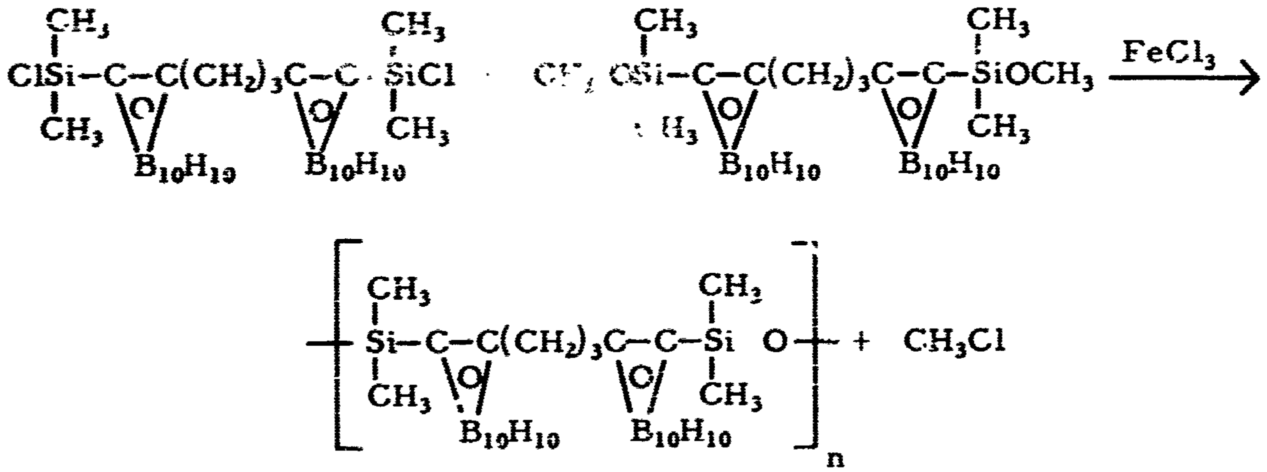
A preparation conducted with 20 gm of the chloro compound and an excess of trimethoxymethane yielded 12 gm of recrystallized product for a 60% yield. The product, once recrystallized from methanol, melted at 156-158° C. A sample recrystallized from pentane melted at 159.5-160°C.

This methoxy compound has been identified by infrared spectroscopy (Figure 1). A complete elemental analysis is pending.

## B. POLYMER SYNTHESIS

An attempt to polymerize bis(1-chlorodimethylsilyl-_o_-carboran-2-yl) propane by hydrolysis/condensation resulted in hydrolytic cleavage of the silicon carborane bond. To ascertain whether this behavior was peculiar to the chloro compound, where hydrolytic cleavage could be catalyzed by released hydrochloric acid, hydrolysis/condensation of the methoxy derivative was also attempted. Hydrolytic cleavage also occurred in the methoxy compound showing the necessity for a nonhydrolysis type polymerization.

Polymerization was effected by the ferric chloride catalyzed condensation of the chloro and methoxy derivatives (Equation 2).



(2)

The reaction was conducted initially with 2 mole percent ferric chloride catalyst but subsequent additions of catalyst were necessary to complete the reaction. The reaction, conducted at 200-240°C, evolved gas over a 10-hour period which amounted to 122.3 percent of theoretical methyl chloride. Infrared and mass spectral analyses of the evolved gas indicated the presence of methyl ether and methanol, in addition to methyl chloride.

The polymer product was obtained as a brown brittle solid of melting range 170-185°C. It is soluble in hot xylene and precipitates on cooling. It is also soluble in acetone. An infrared spectrum of the polymer (Figure 2) exhibited the absorption peaks expected of the proposed structure.

## C. THERMAL STABILITY CHARACTERIZATION

Thermal characterization of the carborane siloxane polymer by DTA and TGA in both air and nitrogen shows it to be thermally stable to 350°C with no oxidation evident until over 400°C. The TGA's in both air and nitrogen (Figures 3 and 4) show first significant weight loss at 350°C. 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 5 and 6) show an exotherm, which is attributable to 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

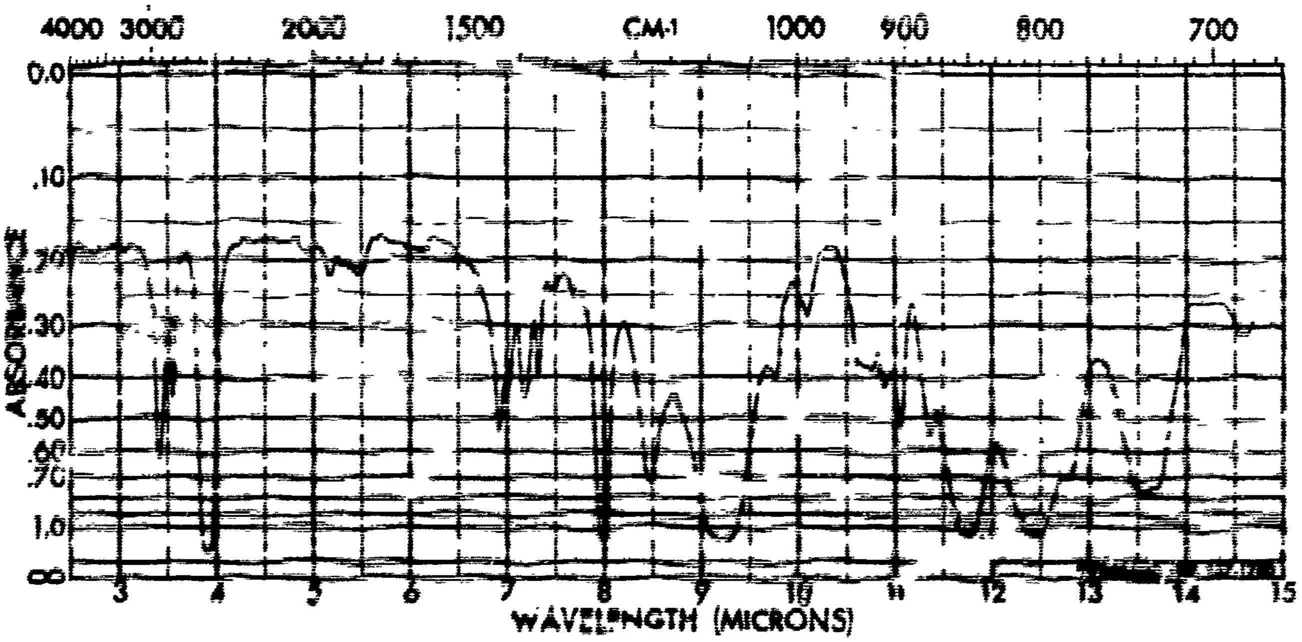


Figure 1. Infrared Spectrum of Bis(1-methoxydimethylsilyl-o-carboran-2-yl]-propane

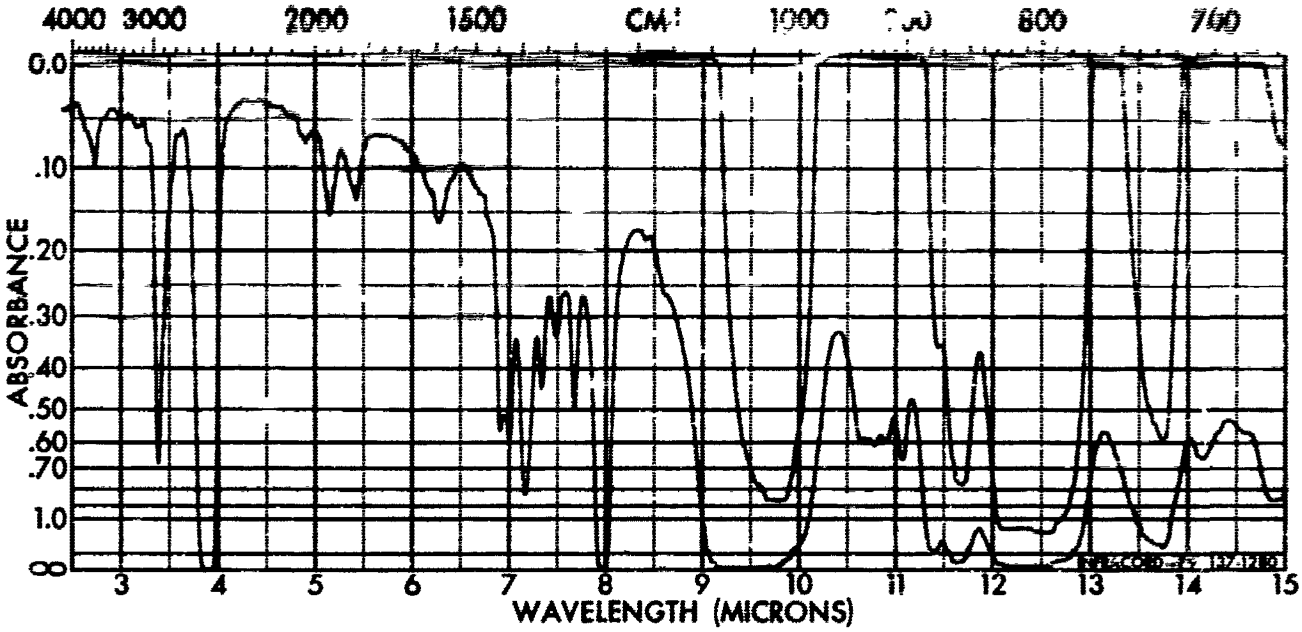


Figure 2. Infrared Spectrum of Carborane Siloxane Polymer

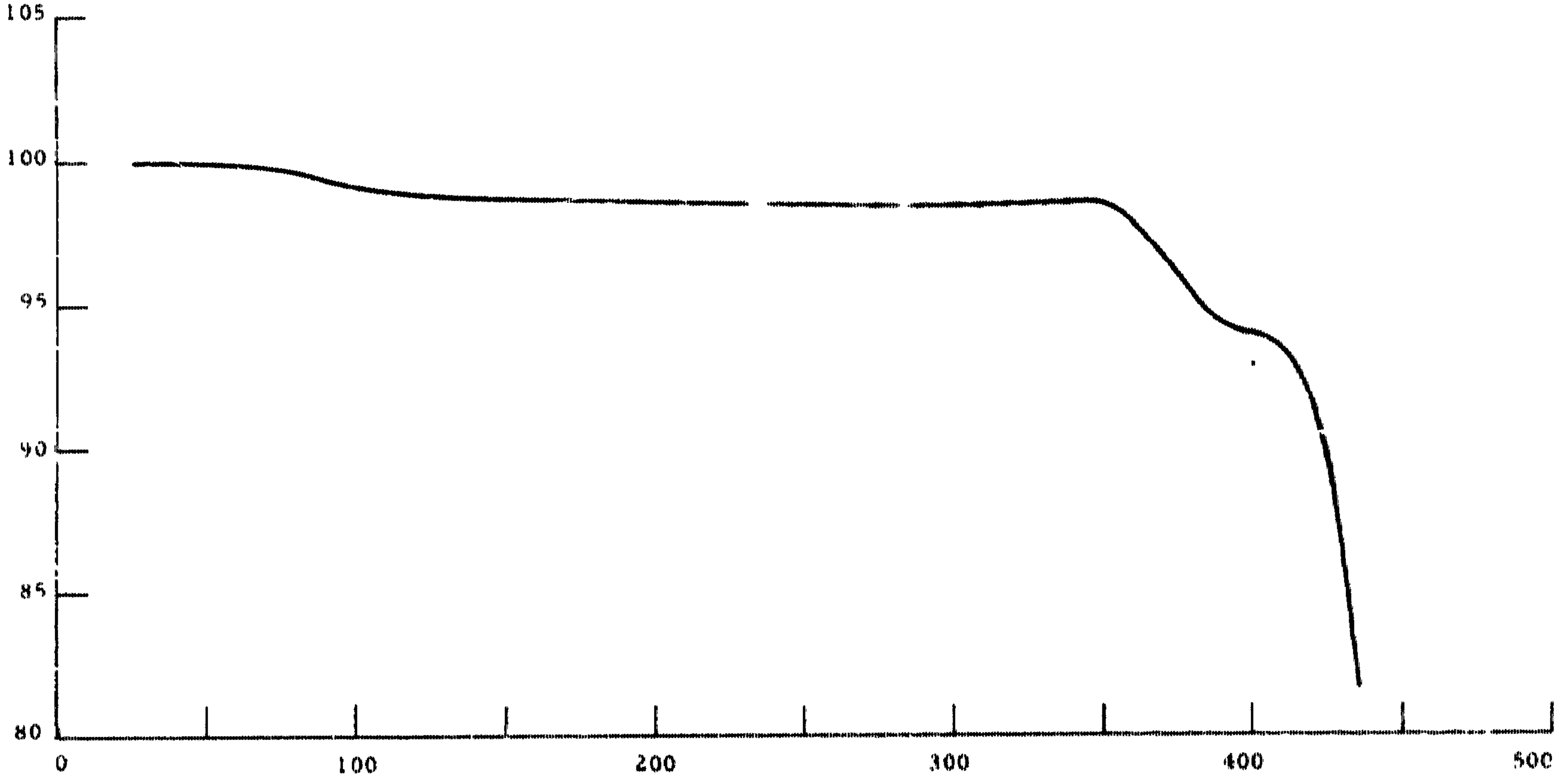


Figure 3. TGA of Carborane Siloxane Polymer in Air

Figure 4. TGA of Carborane Siloxane Polymer in Nitrogen

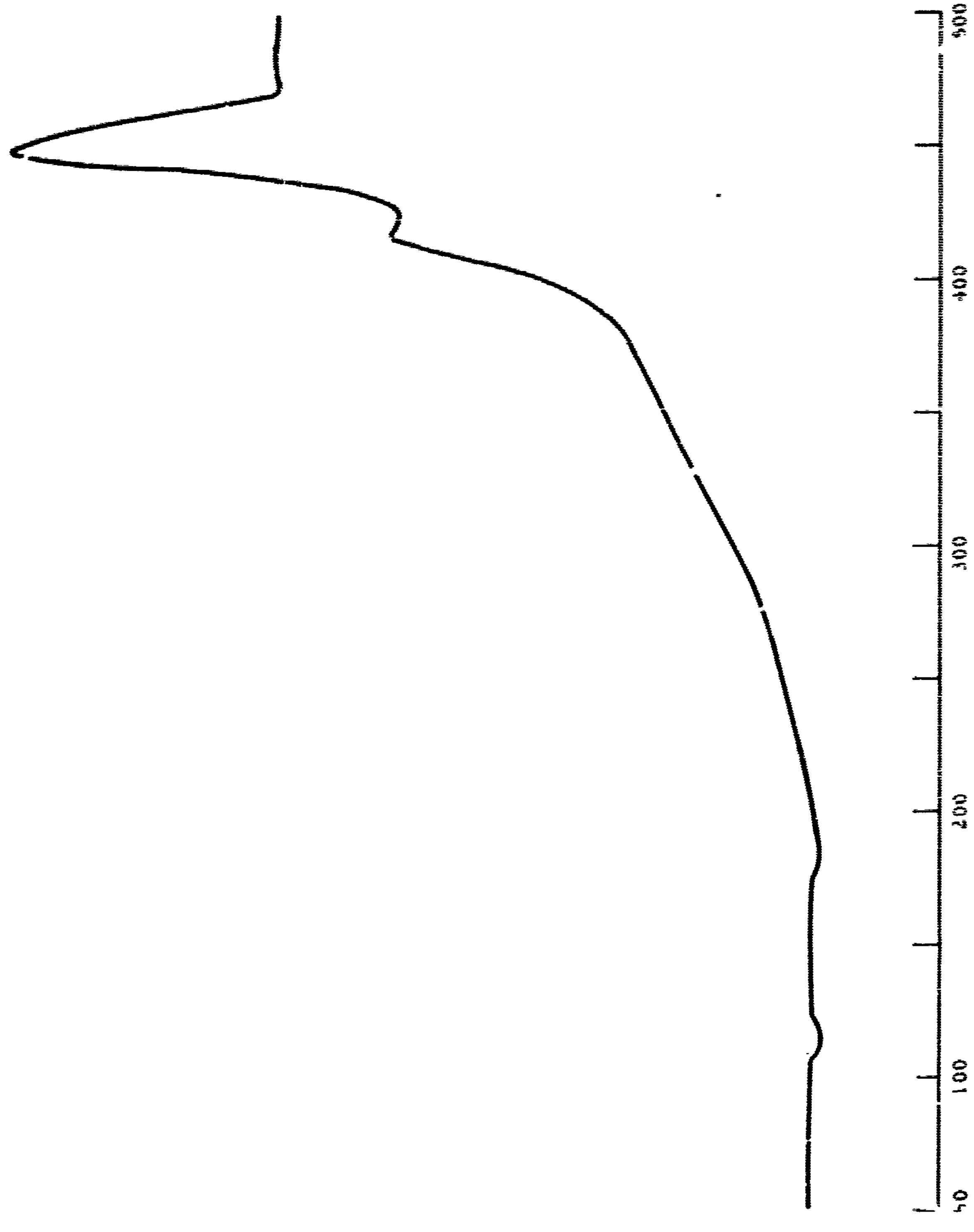


Figure 5. DTA of Carborane Siloxane Polymer in Air

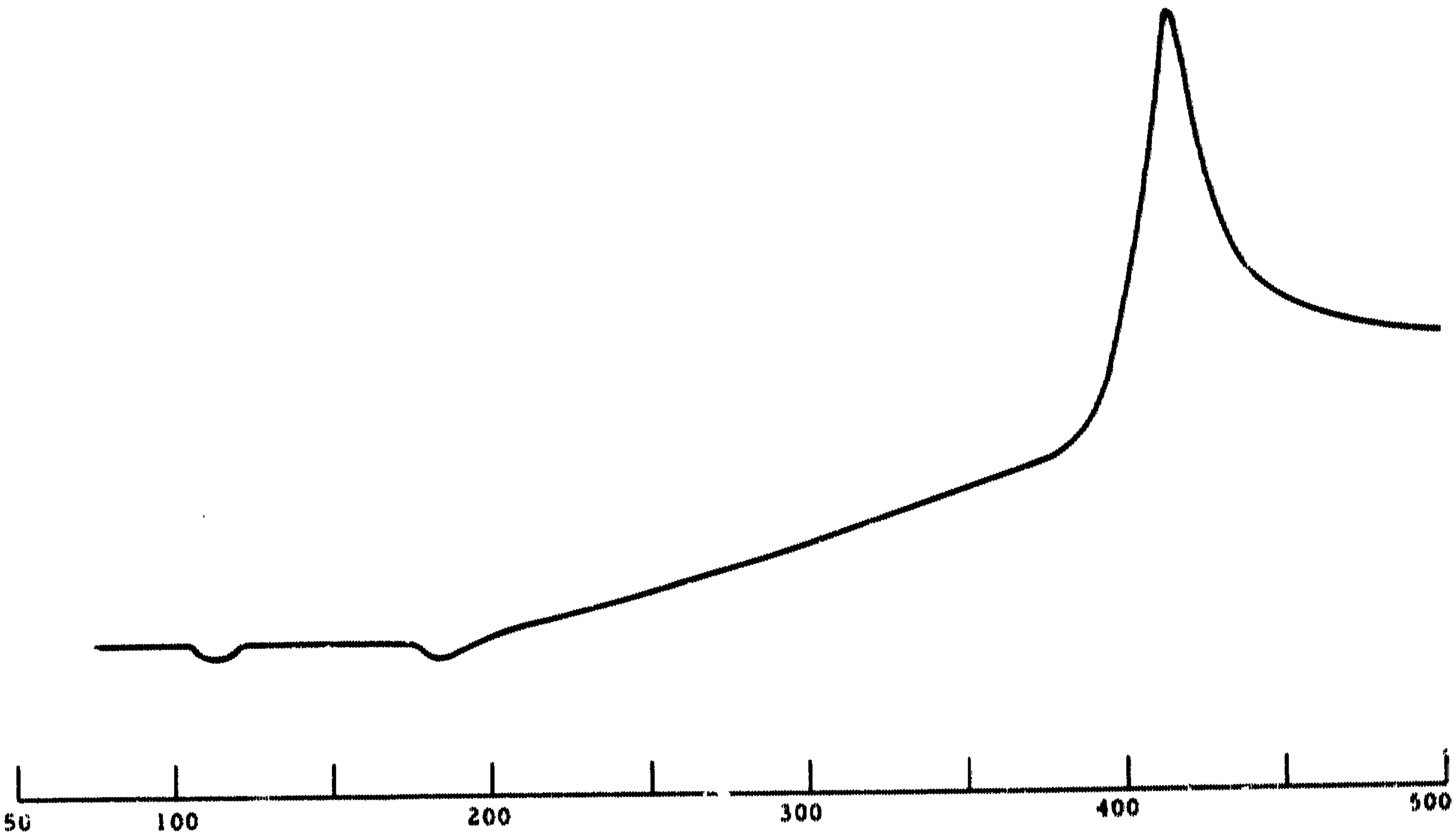


Figure 6. DTA of Carborane Siloxane Polymer in Nitrogen

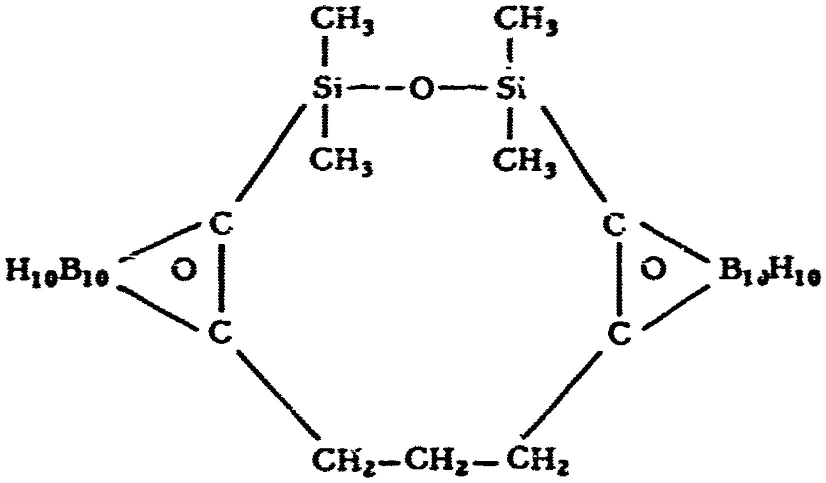
transition, probably the first order transition, since this is in the range of the observed polymer melting temperature. Following the first order transition there is a continuous gradual rise which, since it is not accompanied by any substantial weight loss as shown by the TGA's, may be due to additional polymerization in the molten state or instrument drifting.

## III. DISCUSSION

The polymer that has been prepared is a relatively high melting material (170°C) and probably also has a high glass transition temperature, possibly 110°C. This is evidently a result of chain inflexibility which is caused by the bulky o-carborane moieties. In this polymer, the carboranes are separated by only three carbons and steric interaction of the carborane groups with resultant restrictions on chain bending and coiling may be expected. Such restrictions may be expected in any case where such bulky groups are present in the chain, but the restrictions may be minimized when the groups are adequately separated. The polymers to be prepared which will have as many as five carbons between carboranes are expected to be more flexible and consequently lower melting. Polymers to be prepared which will contain meta- rather than ortho-carborane may also be lower melting. It may be advisable to consider investigating structures that contain linkages between carboranes that are more flexible than methylene chains. Examples of those that could be investigated for their effect on physical properties, their thermal stability and their possible stabilization by carborane are ether, thioether and disulfide linkages.

The concept which has been investigated here (that carborane can stabilize proximate silyl methyl groups to thermal oxidation) has been supported by the thermal character of the polymer most recently prepared. This polymer, which contains carborane adjacent to every silyl methyl group, exhibits first thermal oxidation at 410°C. This is in contrast to the carborane siloxane polymer previously prepared on this program in which the carboranes were three carbon atoms removed from every silyl methyl group. This polymer exhibited thermal oxidative degradation at 240°C (similar to polydimethylsiloxane). The site of the degradation is presumably the silyl methyl groups. Relocation of the carboranes to place them next to all silyl methyl groups has increased thermal oxidative stability from 240° to 410°C and has demonstrated the "protective action" of the carborane.

Both carborane siloxane polymers have exhibited a nonoxidative thermal degradation at about 350°C. A reasonable explanation for the degradation of the first polymer prepared was that it degraded to a cyclic siloxane which was known to exist. The similar thermal degradation of the second polymer at about 350°C may indicate that cyclization also occurs here and that the cyclic of structure VII can exist.

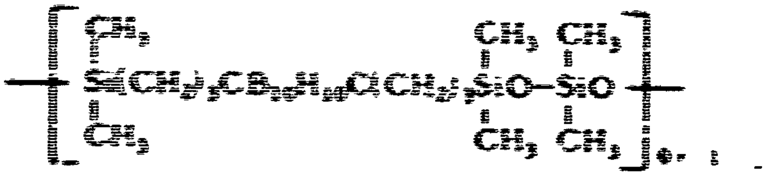


VII

If upon further investigation it is ascertained that degradation does occur in this manner, the ultimate thermal stability limits may be substantially increased by structural changes in the polymer that will prevent cyclization. One example of such a change is the substitution of _meta_-carborane for _ortho_-carborane.

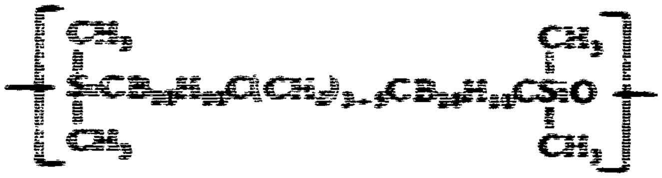
# IV. SUMMARY

The objective of this program is the preparation of a thermally stable carborane siloxane elastomer. The original approach taken to achieve the objective was the preparation of polymers of structure



$$-\left[\overset{CH_3}{\underset{CH_3}{Si}}(CH_2)_3CB_{10}H_{10}C(CH_2)_3\overset{CH_3}{\underset{CH_3}{Si}}O-\overset{CH_3}{\underset{CH_3}{Si}}O\right]_n-$$

However, polymers of such structure were found to be susceptible to thermal oxidation. As a result, the approach was changed, with the new objective being the preparation of polymers of structure



$$-\left[\overset{CH_3}{\underset{CH_3}{Si}}CB_{10}H_{10}C(CH_2)_{3-5}CB_{10}H_{10}C\overset{CH_3}{\underset{CH_3}{Si}}O\right]-$$

which could be more stable to thermal oxidation through stabilization of silyl methyl groups and alkyl linking groups by the inductive or energy sink effect of nearby carborane groups.

The monomers, bis(1-chlorodimethylsilylcarboran-2-yl)propane and bis-(1-methoxydimethylsilylcarboran-2-yl)propane were synthesized and copolymerized with ferric chloride catalyst to yield a polymer of melting temperature of 170°C. TGA and DTA determinations in air and nitrogen show a possible 110°C second order transition temperature for the polymer and show that it is thermally stable to 350°C with no oxidation evident until ca. 400°C.

Comparison of the thermal oxidative stability of this polymer with that of a polymer of similar structure (but which has carborane in a different position in the backbone relative to silicon) shows that carborane does stabilize nearby silyl methyl groups toward thermal oxidation.

## V. REFERENCES

1. S. Papetti, B.S. Schaeffer, A.P. Gray and T.L. Heying, "ACS Polymer Preprints," 6, 1110, September 1965

2. Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, Report RMD 5065-Q4, Contract No. DA-11-070-AMC-852(W), February 1966

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13. ABSTRACT

The carborane silane monomers, bis(1-chlorodimethylsilyl-o-carboran-2-yl) propane and bis(1-methoxydimethylsilyl-o-carboran-2-yl)propane, were synthesized and copolymerized to a carborane polysiloxane. Thermal characterization of the polymer by TGA and DTA in air and nitrogen indicated thermal stability to 350°C with no oxidation evident until over 400°C. The thermal data illustrate the "protective action" of carborane and its ability to stabilize neighboring groups to thermal oxidative degradation.

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