Report RMD 5065-Q6

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

AD 637858

CARBORANE - SILOXANE ELASTOMERS

Report Period: 19 May through 18 August 1966

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Thiokol
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CARBORANE SILOXANE ELASTOMERS

RMD Report 5065-Q6

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

Report Period: 19 May through 18 August 1966

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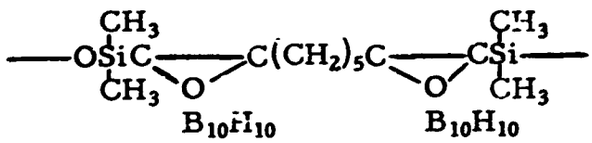
FOREWARD

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 sixth quarter of the program during the period 19 May through 18 Agust 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 compound 1,5-di-o-carboranylpentane and the derivatives 1,5-bis(1-chlorodimethylsilyl-o-carboran-2-yl)pentane and 1,5-bis(1-methoxydimethylsilyl-o-carboran-2-yl)pentane were synthesized. A polymer containing the recurring unit  was prepared by the heterofunctional condensation of the above derivatives, and its thermal and physical properties were characterized.

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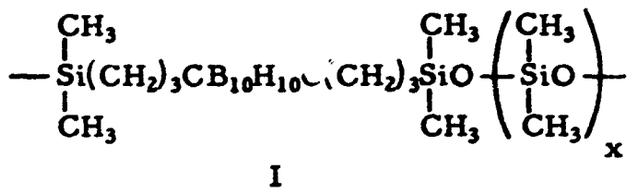
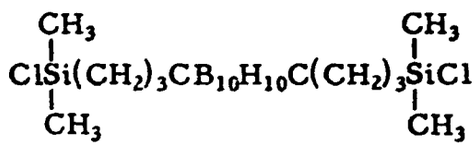
I. INTRODUCTION

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.



I

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



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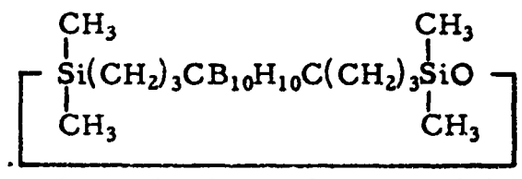

both of which were polymerized to polymers of the desired structures. The polymers were obtained as gums of molecular weights 5000-8500 and higher. The higher polymers did not dissolve and molecular weights are not known, but these materials were tough elastomeric gums of apparently high molecular weight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

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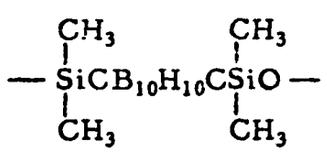
* $-CB_{10}H_{10}C-$ denotes 1, 7-dicarbaclovododecaborane commonly called: m-carborane

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.



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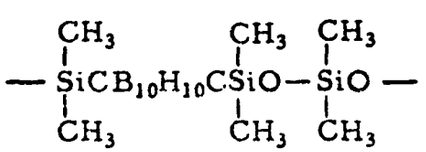

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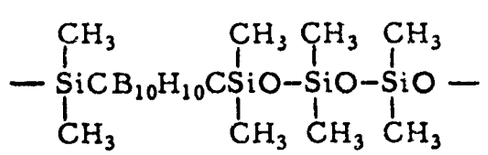

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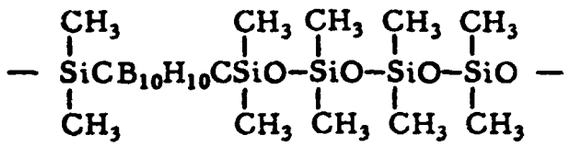
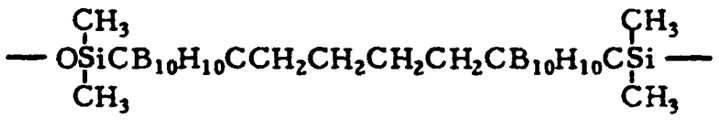


V

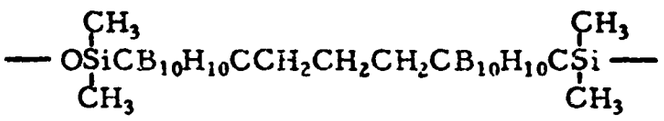
The polymer of structure II., with carborane adjacent to every silicon, exhibited stability to 500°C in an inert atmosphere and to 450°C in air. The polymers of structures III, IV, and V exhibited progressively lower thermal oxidative stabilities. The data indicated that carborane stabilizes adjacent 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.



VI

The first polymer that was prepared to test the hypothesis had the structure VII where the flexible spacer between carboranes was a trimethylene group.



VII

The increased thermal oxidative stability of this polymer indicated that carborane did stabilize the nearby silyl methyl groups toward thermal oxidation, but the lack of any elastomeric character in the polymer indicated that a more flexible spacer between carboranes was necessary. Consequently, the objective during the present report period has been the preparation of the polymer containing a pentamethylene spacer and evaluation of its thermal and physical properties.

II. TECHNICAL PROGRESS

A. PRECURSOR SYNTHESIS

1. 1,5-Di-o-carboranylpentane

The synthesis of dicarboranylalkanes was investigated earlier in this program and has been discussed extensively in a previous report (Ref 2). The compounds of this class previously prepared were 1,3-di-o-carboranylpropane and 1,4-di-o-carboranylbutane. These were obtained by carboranylation of the diacetylene precursor. The carboranylation reaction gave low yields (ca. 10%), but rather than expend considerable effort in a process development study, this reaction was also used to prepare 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 1) indicated this to be the dicarboranylalkane.

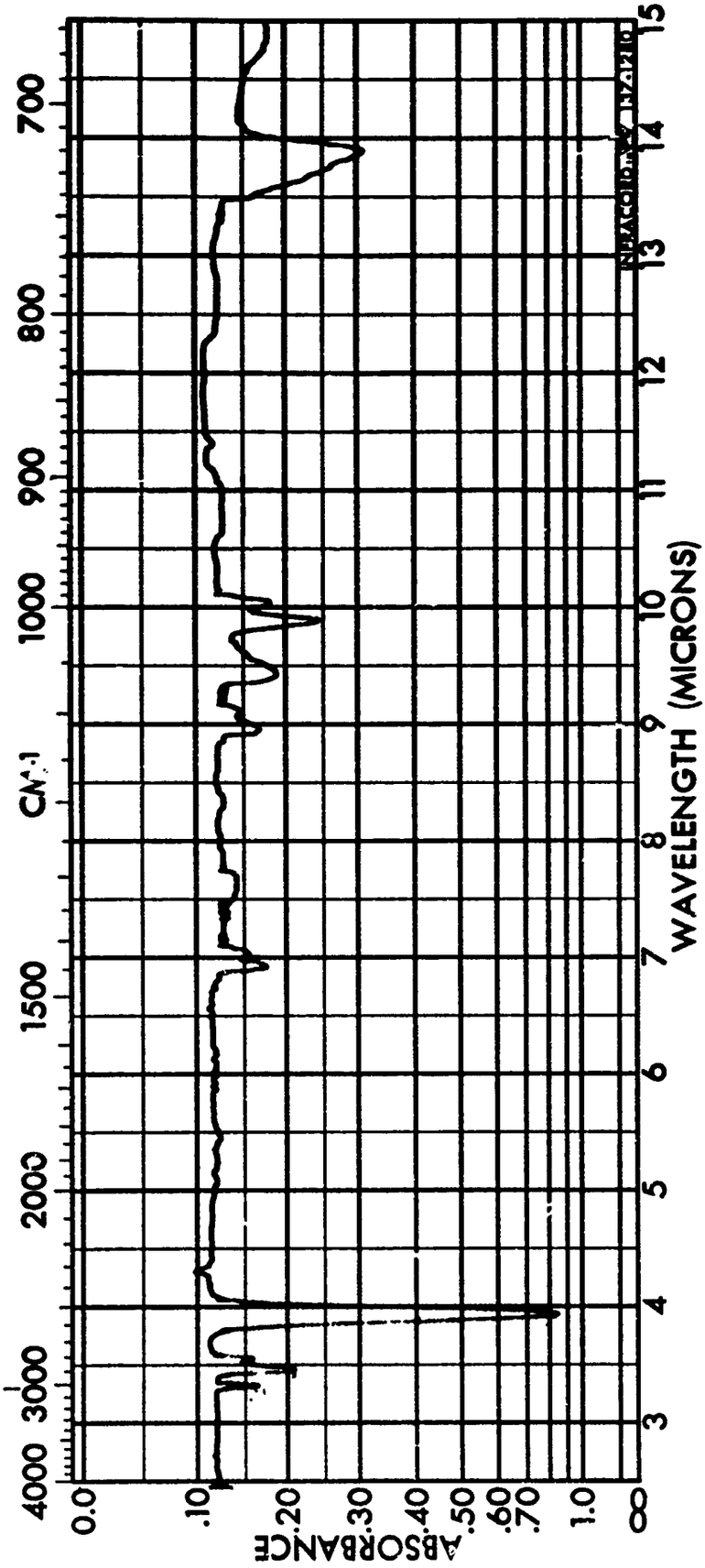


Figure 1. Infrared Spectrum of 1,5-Di-o-carboranylpentane

The distilled liquid is a saturated alkyl carborane, probably heptylcarborane. This is indicated by the infrared spectrum (Figure 2) 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 by-products of the reaction. Support for this view is found in the preparation of isopropylcarborane by the reaction of isopropenylcarborane with the solid by-product obtained from the preparation of isopropenylcarborane from decaborane, acetonitrile, and isopropenylacetylene (Ref 3). 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.

B. MONOMER SYNTHESIS

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

This material was synthesized in the manner previously described for the propane derivative (Ref 2, 4). Specifically, 29.4 gm of 1,5-di-o-carboranylpentane dissolved in 500 ml of ethyl ether was allowed to react with 11.6 gm of butyllithium in hexane solution to obtain the dilithiated dicarboranylpentane, which was then added as a slurry to a large excess of dichlorodimethylsilane. The crude yield of silylated carborane product, after removal of lithium chloride by filtration and evaporation of volatiles, was 39.3 gm (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 [illegible]on 113, was obtained as crystals of mp 139.5-141°C. The infrared spectrum (Figure 3) was almost identical to that of the propane derivative (Ref 4).

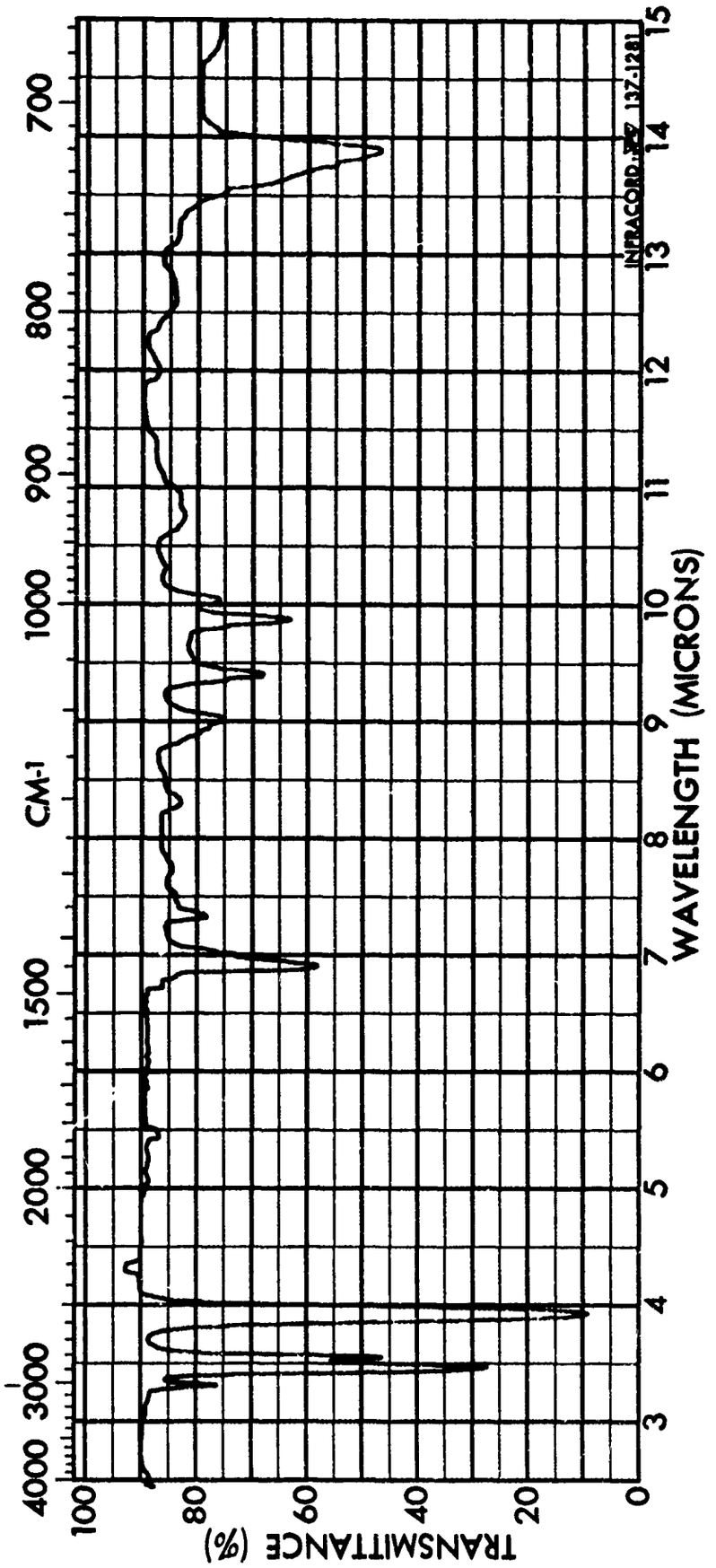


Figure 2. Infrared Spectrum of "n-Heptylcarborane"

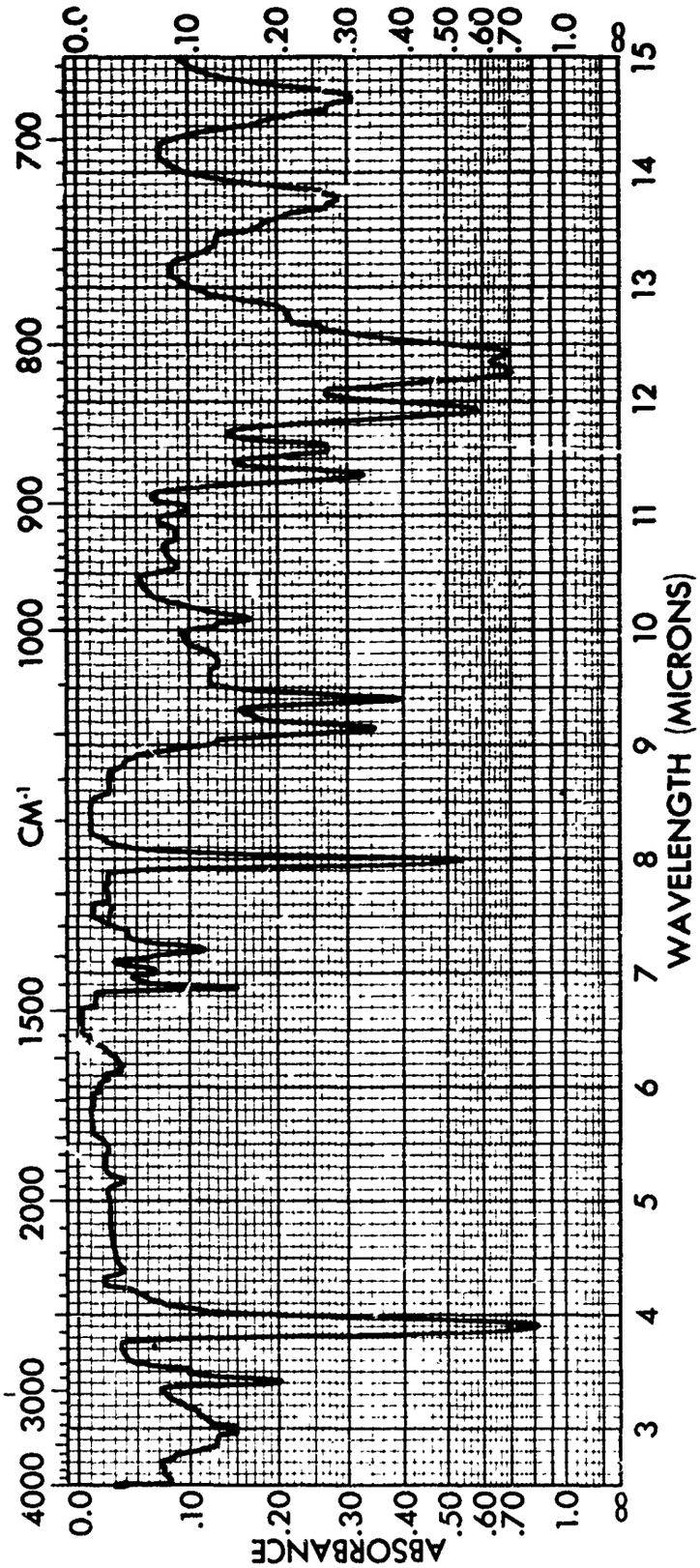


Figure 3. Infrared Spectrum of 1,5-Bis(1-chlorodimethylsilyl-o-carboran-2-yl)pentane

2. 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 4) exhibits an absorption at 9.2 microns, which is indicative of the SiOC bonding of the methoxy derivative.

C. POLYMER SYNTHESIS

Polymerization of silyl-o-carborane compounds was accomplished in previous work by the ferric chloride catalyzed condensation of silylchloride and silylmethoxy groups (Ref 4). This procedure has been used again for the polymerization of 1,5-bis(1-chlorodimethylsilylcarboran-2-yl) pentane and 1,5-bis(1-methoxydimethylsilylcarboran-2-yl)pentane. The polymerization was investigated before the most effective purification of the chlorosilane compound was accomplished; thus, chlorosilane used here was 90% pure as determined by titration with aqueous sodium hydroxide in an ethanol-acetone-water media. The monomers, in stoichiometric proportions, were heated with 1.0% anhydrous ferric chloride at 200°C for 24 hours, yielding a soft, black, gum product. The polymer was separated from the catalyst residue by extraction of the polymer with hot xylene and treatment of the xylene solution with hexane to precipitate the catalyst. The polymer, after evaporation of the solvents, remained as a clear, brown gum. The infrared spectrum of the polymer (Figure 5), with absorption maxima at 9.35 and 9.75 microns for SiOSi and the absence of an absorption at 14.6 microns for SiCl, indicates the

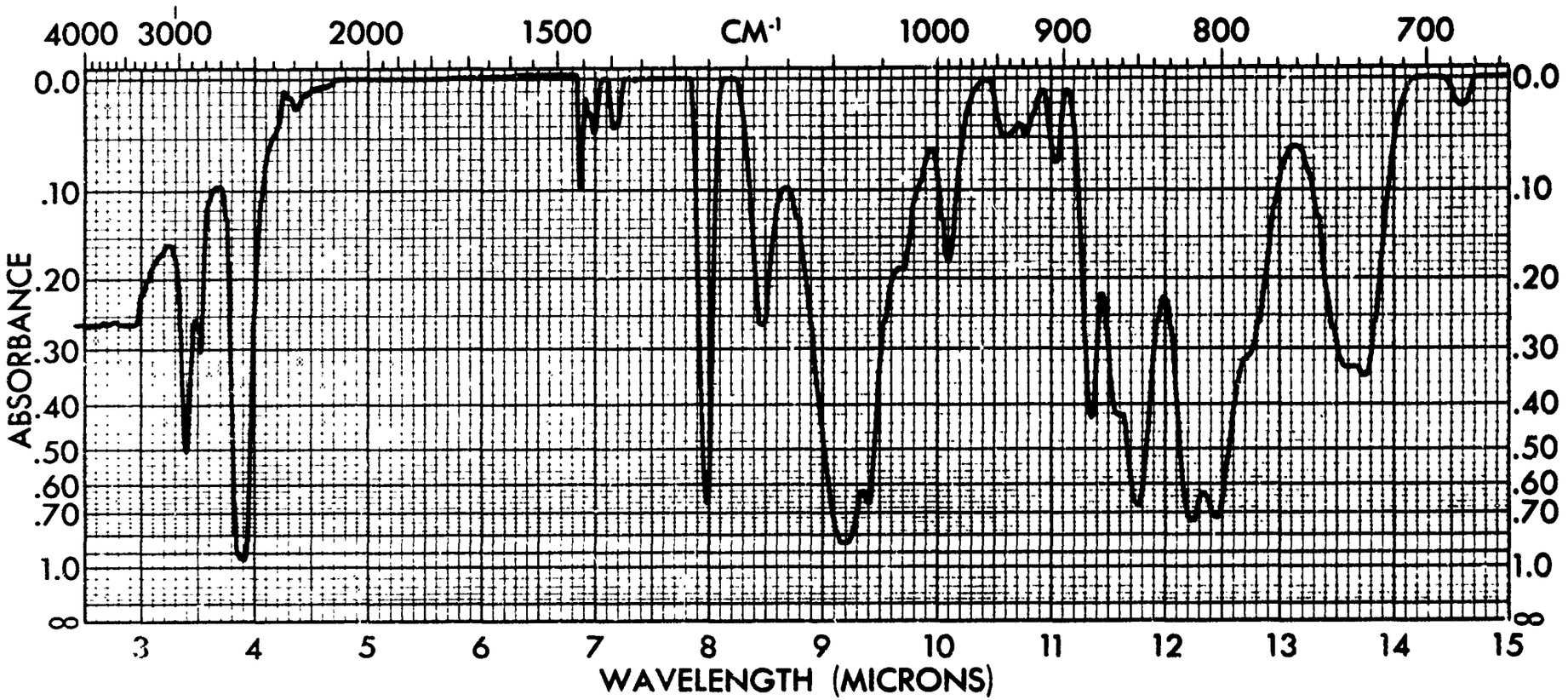


Figure 4. Infrared Spectrum of 1,5-Bis(1-methoxydimethylsilyl-o-carboran-2-yl)pentane

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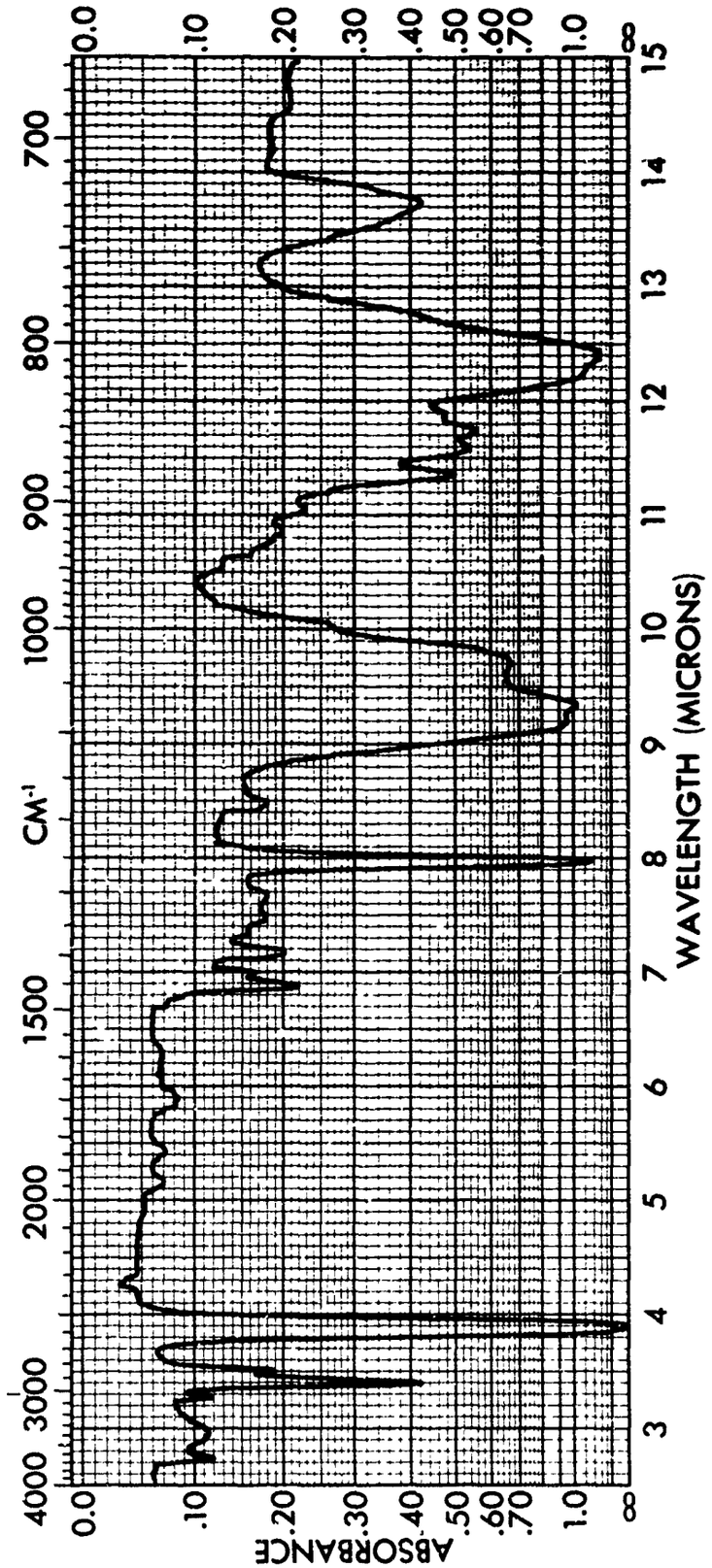


Figure 5. Infrared Spectrum of Dicarboranylpentane Polysiloxane

siloxane polymer structure. A small absorption of 3.27 microns shows the presence of carborane CH and suggests that this low molecular weight polymer is at least partially terminated with monosubstituted carborane material that was present in the monomers as an impurity. The molecular weight of the polymer was not determined but is estimated to be near that of the 1,3-dicarboranylpropane polymer prepared previously, which had a molecular weight of 4000.

D. THERMAL STABILITY CHARACTERIZATION

TGA's of the dicarboranylpentane siloxane polymer in nitrogen and air show decomposition beginning at about 250°C (Figures 6 and 7). 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 8 is a modified drawing of the DTA curves). 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 dicarboranylpropane polymer (prepared previously) 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 dicarboranylpentane polymer at 350°C probably is due to the pentane groups.

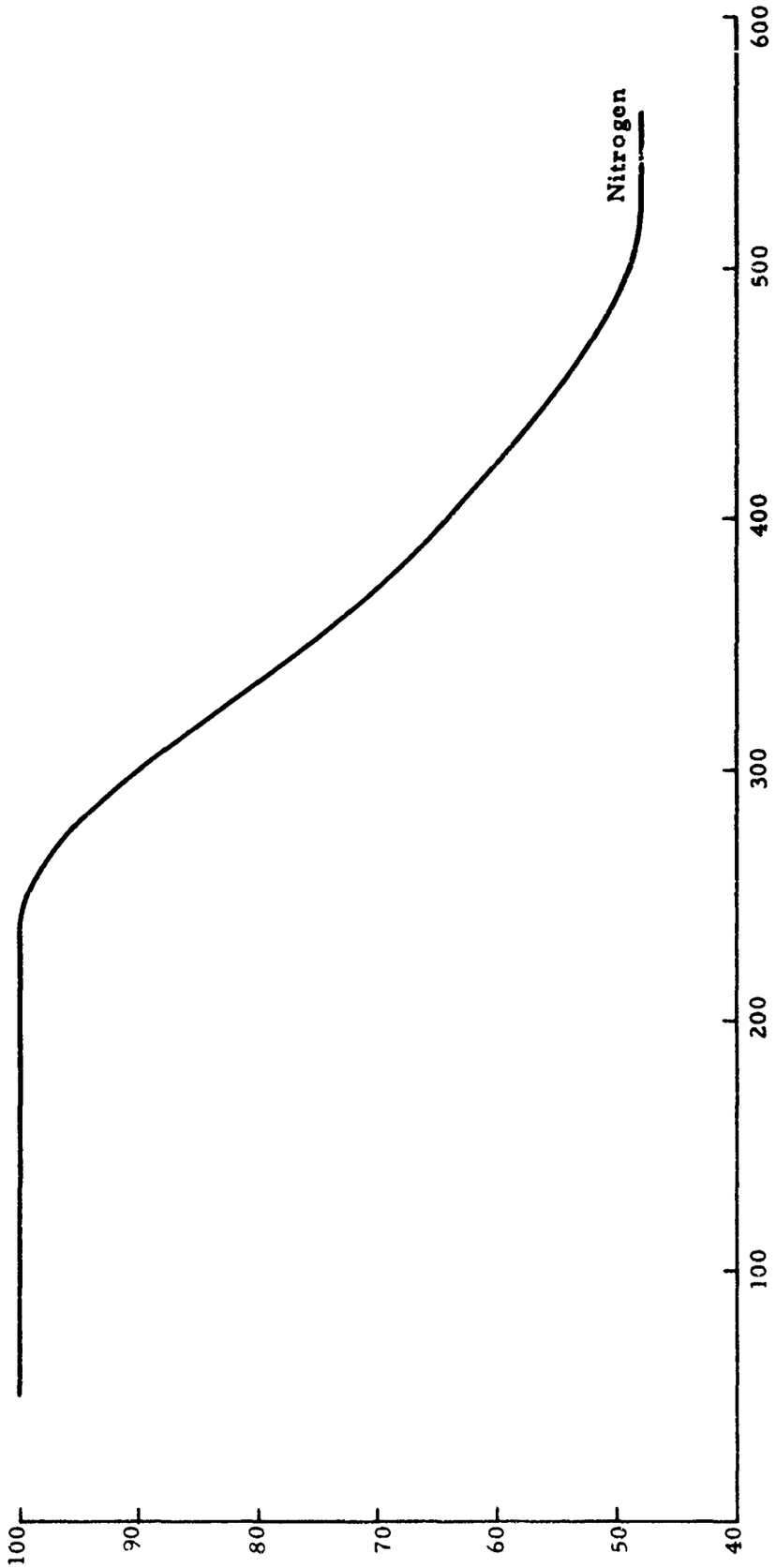


Figure 6. TGA of Dicarboranylpentane Polysiloxane in Nitrogen

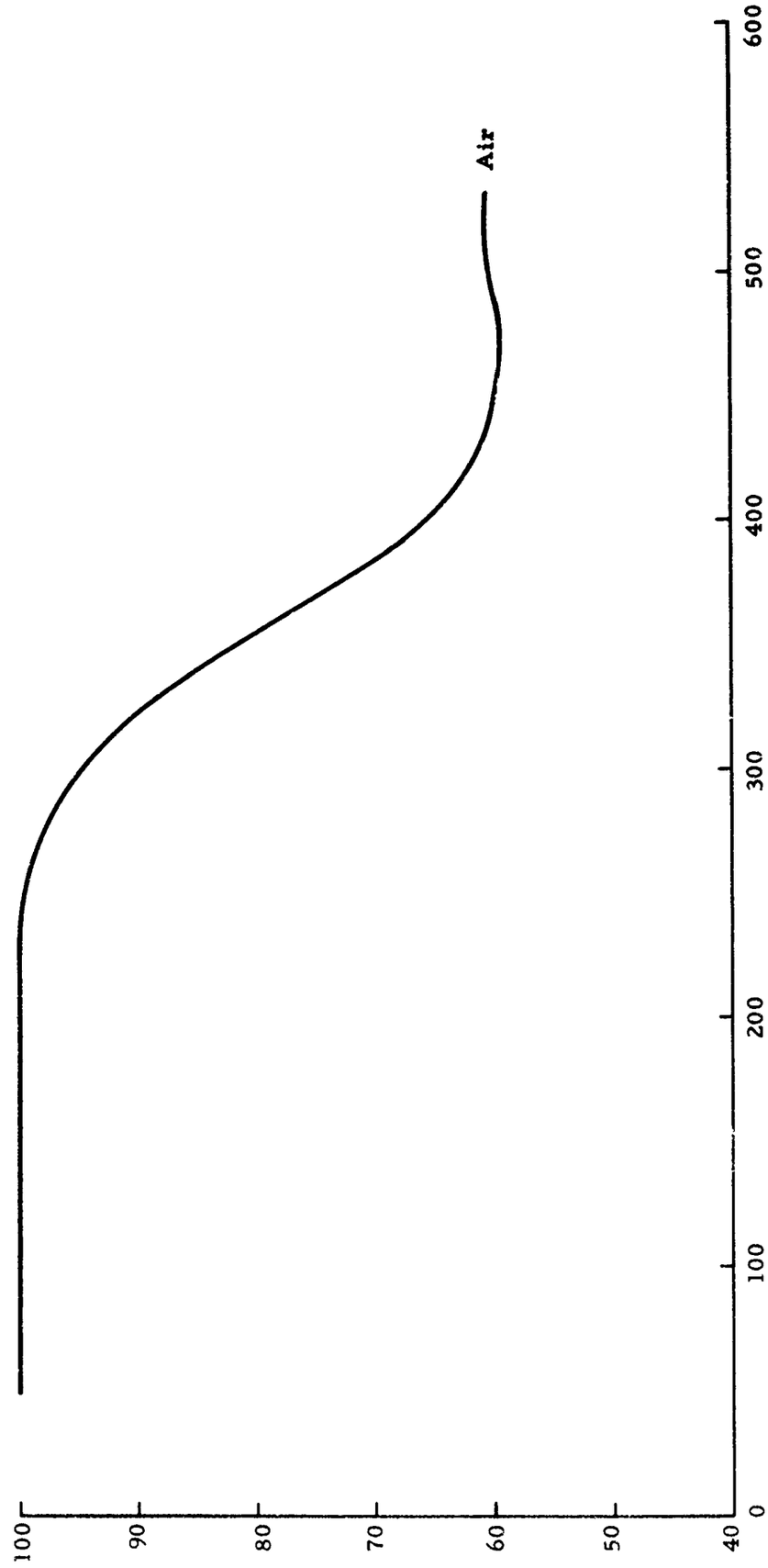


Figure 7. TGA of Dicarboranylpentane Polysiloxane in Air

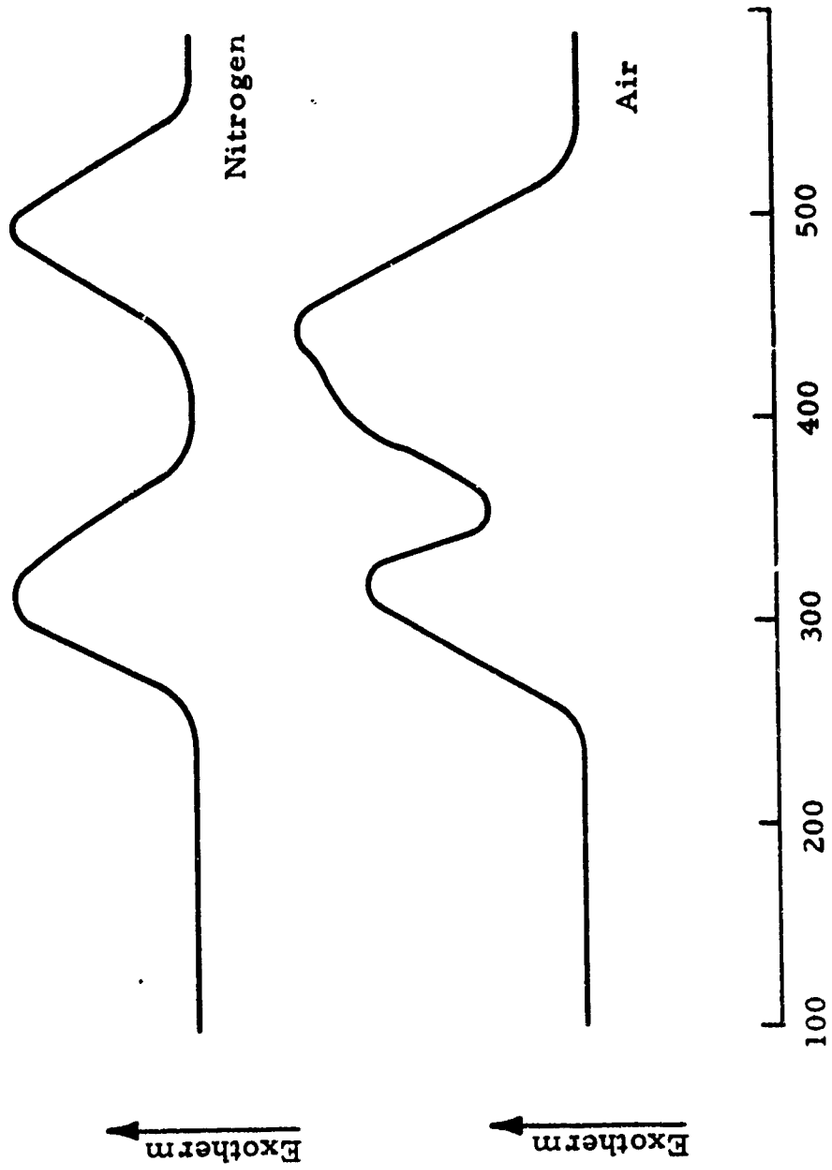


Figure 8. DTA of Dicarboranylpentane Polysiloxane in Air and Nitrogen

III. DISCUSSION

The dicarboranylpropane polysiloxane prepared previously demonstrated that carborane stabilized the polymer toward thermal oxidation, presumably by protecting the hydrocarbon portions of the polymer that vere within the carborane's "sphere of influence." This polymer underwent thermal oxidation at about 410°C and a nonoxidation degradation at 350°C. However, the polymer was high melting (170°C), and the dicarboranylpentane polysiloxane was prepared in an effort to lower the melting temperature and increase nonoxidative thermal stability.

The dicarboranylpentane polysiloxane has demonstrated the expected drop in melting temperature and, in fact, is a gum that could be an elastomer at high molecular weights. This polymer, however, has even lower nonoxidative thermal stability than the propane polymer and also has reduced oxidative thermal stability. The decrease of nonoxidative thermal degradation temperature from 350° to 250°C was unexpected,particularly because decomposition through cyclic formation should have been inhibited by the longer polymer unit length of the pentane polymer. That this did not occur is indication that decomposition, at least for the pentane polymer, is not through cyclic formation. The lower oxidative thermal stability is a consequence of extending the hydrocarbon portion of the polymer beyond the carborane's protective influence. The pentane groups, which are necessary for chain flexibility and the required physical properties, cause lower overall polymer thermal stability.

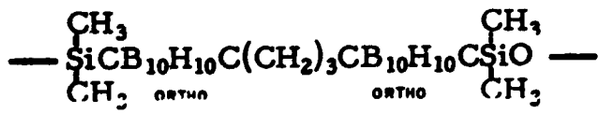
It has now been ascertained that a propane spacer group between carboranes is stable but not flexible and that a pentane group is flexible but not stable. We expect that a butane spacer would be intermediate in these properties, but that the probability of gaining the desired combination of properties with a butane spacer is small. However, since it has been demonstrated that carborane does stabilize the silylmethyl groups, it remains to find a thermally stable, flexible, spacer group for the carboranes in order to achieve the desired polymer. Of the number of groups that may be investigated for this purpose, including ether, thioether, disulfide, fluorocarbon alkane and fluorocarbon ether, we believe that the thermally stable fluorocarbon types are most feasible.

The future work of this program thus will be directed toward the preparation of carborane polysiloxanes with fluorocarbon alkane and fluorocarbon ether spacer groups between carboranes. It is anticipated that synthesis of such polymers may be accomplished — and possibly facilitated — by the use of m-carborane as well as o-carborane and, thus, the effects of the meta isomer on polymer physical and thermal properties may also be ascertained.

IV. SUMMARY

Previously, the preparation and evaluation of polymers of structures I and VII has shown that such polymers did not possess the combination of properties necessary for a thermally stable elastomer.

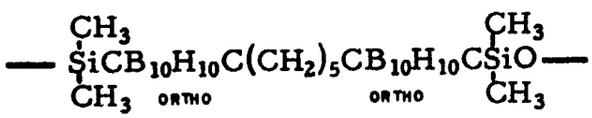
I



VII

Polymer of structure VII had good thermal properties but poor physical properties.

Preparation and evaluation of polymer of structure VIII was done in an attempt to improve physical properties and maintain thermal stability.



VIII

The polymer physical properties were improved to the extent that elastomeric character would be expected in a high molecular weight polymer, but TGA and DTA showed the polymer to be of inferior thermal stability.

It is anticipated that carborane siloxane polymers of structures similar to VII and VIII, but containing fluorocarbon alkane or fluorocarbon ether spacer groups between carboranes, may have the desired combination of properties. The future work of the program will be directed toward these objectives.

V. REFERENCES

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2. Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, Report RMD 5065-Q4, Contract No. DA-11-070-AMC-852(W), February 1966.
3. Carl D. Ross, (to Callery Chemical Company) U.S. 3,028,432 (1962)
4. Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, Report RMD 5065-Q5, Contract No. DA-11-070-AMC-852(W), May 1966

UNCLASSIFIED
Security Classification

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(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Thiokol Chemical Corporation Reaction Motors Division Denville, New Jersey	2a. REPORT SECURITY CLASSIFICATION Unclassified 2b. GROUP NA

3. REPORT TITLE

CARBORANE-SILOXANE ELASTOMERS

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

Quarterly Progress Report, 19 May to 18 August 1966

5. AUTHOR(S) (Last name, first name, initial)

Mayes, Nathan

6. REPORT DATE August 1966	7a. TOTAL NO. OF PAGES 25	7b. NO. OF REFS 4
8a. CONTRACT OR GRANT NO. DA-11-070-AMC-852(W) b. PROJECT NO 5065 c. d.	9a. ORIGINATOR'S REPORT NUMBER(S) RMD 5065-Q6 9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report) None	

10. AVAILABILITY/LIMITATION NOTICES

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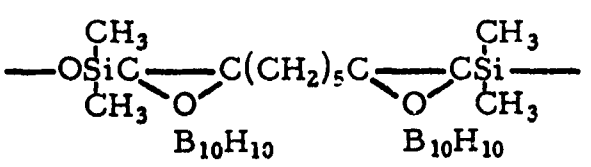
11. SUPPLEMENTARY NOTES None	12. SPONSORING MILITARY ACTIVITY Rock Island Arsenal, Rock Island, Illinois

13. ABSTRACT

The compound 1,5-di-o-carboranylpentane and the derivatives 1,5-bis(1-chlorodimethylsilyl-o-carboran-2-yl)pentane and 1,5-bis(1-methoxydimethylsilyl-o-carboran-2-yl)pentane were synthesized. A polymer containing the recurring unit



was prepared by the heterofunctional condensation of the above derivatives, and its thermal and physical properties were characterized.

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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
Carborane						
Polysiloxane						
Dicarboranylalkane						
Thermally Stable Polymer						

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