

CARBORANE - SILOXANE ELASTOMERS

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CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVER, NEW JERSEY

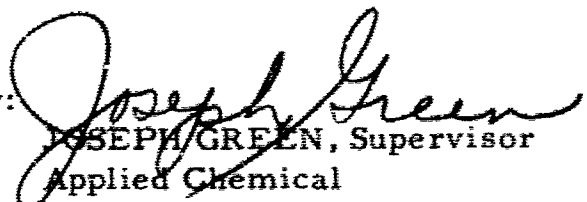
CARBORANE-SILOXANE ELASTOMERS

RMD Report 5065-Q3

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

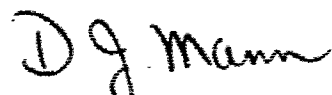
Report Period: 19 August 1965 through 18 November 1965

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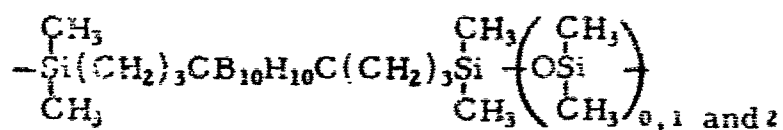
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FOREWORD

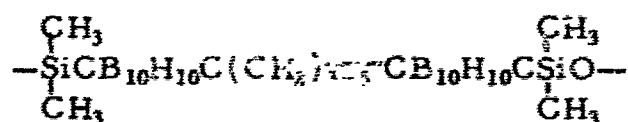
This report was prepared by Thiokol Chemical Corporation, Reaction Motors Division, under U. S. Army Contract No. DA-11-070-AMC-852 (W). It covers work done in the third quarter of the program during the period 19 August 1965 through 18 November 1965. Mr. Z. T. Ossefort of Rock Island Arsenal is the project Engineer. Contributors at Thiokol are Mr. Nathan Mayes (Principal Scientist) and Mr. Alan Jackson.

ABSTRACT

Polymers of structure



were found to be susceptible to thermal oxidation at about 240° C. Materials of structure



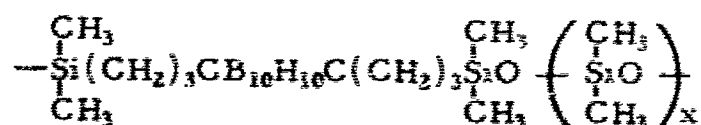
are expected to resist thermal oxidative attack due to the stabilization of silyl methyl groups by carborane. An investigation of the preparation of precursors having the structures $\text{HCB}_{10}\text{H}_{10}\text{C}(\text{CH}_2)_3\text{CB}_{10}\text{H}_{10}\text{CH}$ was initiated and compounds with 3 and 4 methylene groups have been prepared.

CONTENTS

	Page
I. INTRODUCTION	.
II. TECHNICAL PROGRESS	
A. Monomer Synthesis	4
B. Polymer Synthesis	6
III. SUMMARY	8
IV. REFERENCES	9

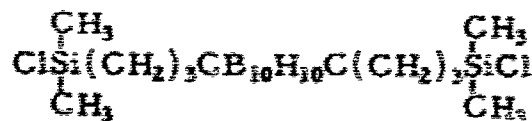
I. INTRODUCTION

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 of structure* I where x = 0, 1, and 2.

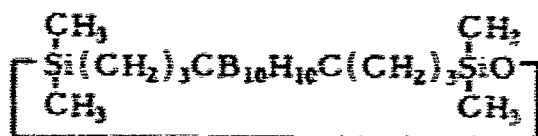


I

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



and

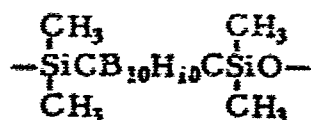


both of which were polymerized to polymers of the desired structures. The polymers were obtained as gums of molecular weights 5000-8500 and higher. The higher polymers did not dissolve and molecular weights are not known, but these materials were tough elastomeric gums of apparently high molecular weight.

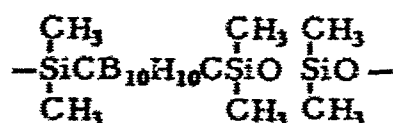
* $-\text{CB}_{10}\text{H}_{10}\text{C}-$ denotes 1,7-dicarbavododecaborane commonly called m-carborane.

Evaluations of polymer of structure I ($x = 0$) for thermal and thermal oxidative stability indicated stability in inert atmosphere to 370°C but decomposition in air at 240°C . 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 re-examine the approach that had been taken and to consider altering the course of the program.

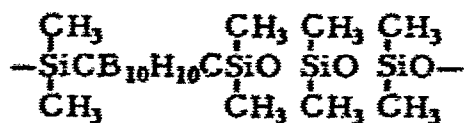
The reason for the lack of thermal oxidative stability in the polymer under discussion became apparent upon examination of some recently published work concerning carborane siloxane polymers of somewhat different structure (Ref 1). These polymers, with structures II, III, IV, and V, contained carborane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



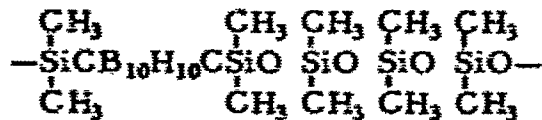
II



III



IV

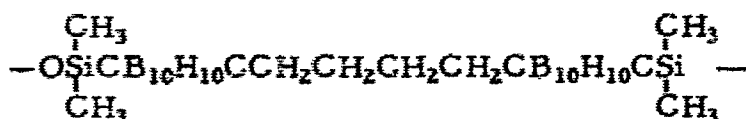


V

Polymer of structure II, with carborane adjacent to every silicon, exhibited stability to 500°C in 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 further 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 carborane is too far removed 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 I, however, is a high melting resin (mp $>200^{\circ}\text{C}$) 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

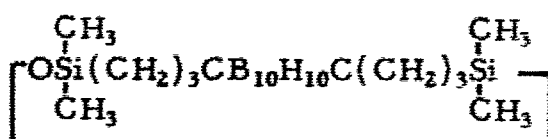
On the basis of the considerations discussed above the course of the program was changed during the third quarter to allow preparation of polymers of structure VI and related structures. New precursors and monomers are required for the new polymers and much of the third quarter has been devoted to the preparation of new carborane precursor materials. Initial exploratory work toward the preparation of new precursors has been with o-carborane derivatives since these are more readily obtained than the m-carborane analogs. In addition, the greater inductive effect of the o-carborane group would be expected to have a greater influence in thermal-oxidative protection.

II. TECHNICAL PROGRESS

A. MONOMER SYNTHESIS

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

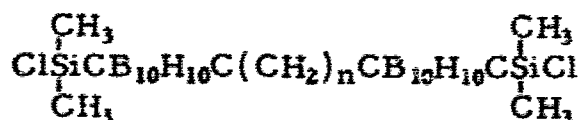
The compound obtained upon hydrolysis of 1,7-bis [3-(chlorodimethylsilyl)propyl] -m-carborane has now been positively identified as the cyclododecane shown below:



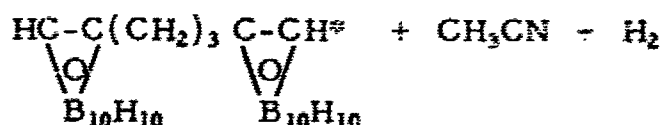
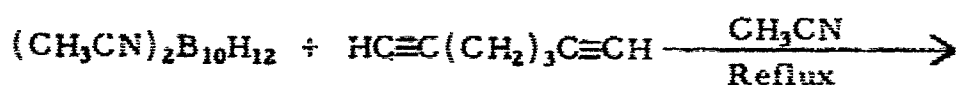
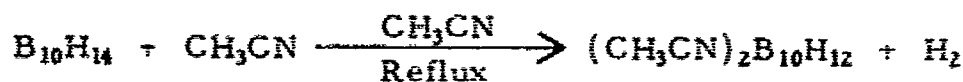
Calculated for $\text{C}_{12}\text{H}_{34}\text{B}_{10}\text{OSi}_2$: C, 40.18; H, 9.55; B, 30.14; Si, 15.66
Found: C, 40.20; H, 9.89; B, 30.00; Si, 16.57

2. 1,3-Di-o-carboranylpropane

Both o- and m-carborane compounds of the type, $\text{HCB}_{10}\text{H}_{10}\text{C}(\text{CH}_2)_3\text{CB}_{10}\text{H}_{10}\text{CH}$, are desired as precursors to silane monomers. The monomers are to be prepared according to the equations below.



The compound, 1,3-di-o-carboranylpropane was prepared according to the following equations:



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 $\text{C}_7\text{H}_{28}\text{B}_{20}$: 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 2). Pyrolysis of di-o-carboranylpropane at 450°C for 24 hours yielded material of mp 295-305°C which showed changes in the infrared spectrum indicative of isomerization to a m-carborane species. As yet, however, all attempts to isolate a pure component from the crude pyrolysis product have failed.

3. 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 carboranylation agent and toluene as solvent, led to a 10% yield of material of

* -C-C denotes o-carborane

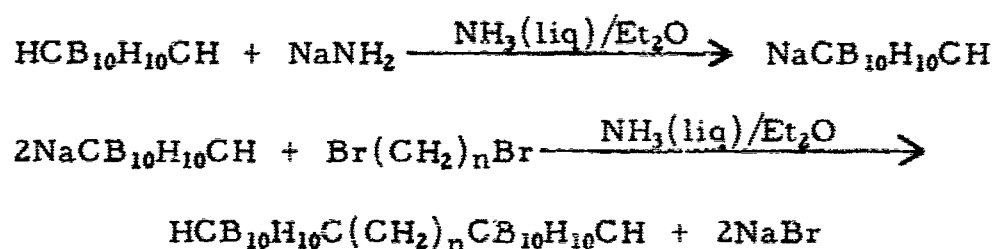


mp 281-283°C. It was identified by infrared and elemental analyses as 1,4-di-o-carboranylbutane.

Calculated for C₈H₃₀B₂₀: C, 28.04; H, 8.83; B, 63.12
Found: C, 28.20; H, 8.89; B, 62.91

The preparation of compounds of the class $\text{HC}-\underset{\text{B}_{10}\text{H}_{10}}{\underset{\text{O}}{\text{C}}}(\text{CH}_2)_n\underset{\text{B}_{10}\text{H}_{10}}{\underset{\text{O}}{\text{C}}}-\text{CH}$ by car-

boranylation of diacetylenes has been successful as noted above; however, these were not efficient reactions and quite low yields were obtained. A potentially better method of obtaining these compounds as well as the analogous m-carborane derivatives is by alkylation of carborane. Such reactions have been reported by Zakharkin (Ref 3) whereby alkylation was achieved by reaction of sodium amide (also lithium and potassium amides) with carborane followed by reaction with an alkyl bromide. How this alkylation may be utilized to obtain the precursors desired on this program is illustrated below.



An investigation of this procedure has been initiated with an attempt to prepare 1,3-di-o-carboranylpropane. There are no results to report at this time.

B. POLYMER SYNTHESIS

The ring-opening polymerization of $\left[\text{OSi} \begin{array}{c} \text{CH}_3 \\ | \\ (\text{CH}_2)_3\text{CB}_{10}\text{H}_{10}\text{C}(\text{CH}_2)_3\text{Si} \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n$

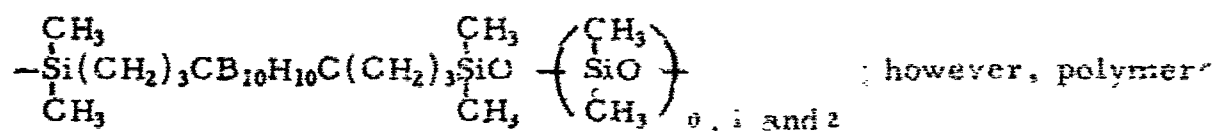
to polymers of about 5000 molecular weight has been reported previously (Ref 4). The catalyst used for the polymerization was concentrated sulfuric acid. It has now been determined that use of concentrated sulfuric acid catalyst in the initial stage of the polymerization followed by dilution with water in the later stage yields a polymer of significantly higher molecular weight. This polymer is no longer soluble in solvents that dissolve the lower molecular product and thus no molecular weight has been determined. Its physical properties, however,

particularly toughness and elasticity, indicate the higher molecular weight. This behavior of concentrated and dilute sulfuric acid has been explained by Andrianov (Ref 5). The concentrated acid very effectively breaks Si-O bonds and initiates ring-opening polymerization. The subsequent dilution of the acid reduces the breakage of Si-O bonds in the growing polymer and allows it to become higher in molecular weight.

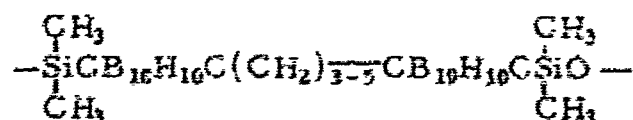
Another catalyst found effective for the ring-opening polymerization was phosphoric acid. This material yielded polymer of 8500 molecular weight. A basic catalyst, potassium hydroxide, was ineffective at all concentrations tried.

III. 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

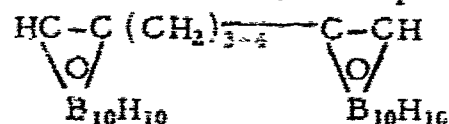


of such structure were found to be susceptible to thermal oxidation. As a result, the approach was changed with the new objective being the preparation of polymers of structure



These polymers may be 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.

Efforts to prepare such polymers have been initiated with an investigation of the synthesis of precursors of the structure $\text{HCB}_{10}\text{H}_{10}\text{C}(\text{CH}_2)_{3-5}\text{CB}_{10}\text{H}_{10}\text{CH}$ where both ortho- and meta- carborane isomers are employed. To date, o-carborane derivatives of structures



have been prepared in low yield reactions. Investigation of these preparations by a potentially high yield reaction has been initiated.

IV. REFERENCES

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3. L. I. Zakharkin, Tetrahedron Letters 1964 (33-34), 2255-8
4. Thiokol Chemical Corporation, Reaction Motors Division, Report RMD 5065-Q2, Contract No. DA-11-020-AMC-852 (W)
5. K. A. Andrianov, Metalorganic Polymers, Interscience Publishers, New York (1965), p. 221

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Carborane Polysilmethylenesiloxanes						
Thermally Stable Elastomers						
Siloxanes						

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