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A Summary

Hansjuergen A. Schroeder

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13. ABSTRACT

The various types of existing carborane-based polymers are broadly surveyed with regard to structures, physical properties, thermal stabilities and end-use applications.

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CARBORANE POLYMERS

by

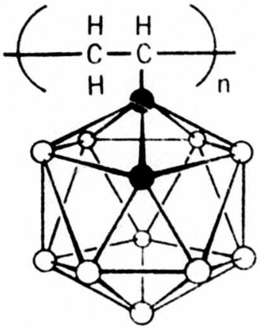
Hansjuergen A. Schroeder
Olin Research Center
New Haven, Connecticut 06504

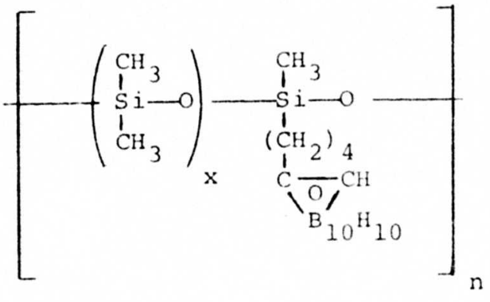
INTRODUCTION

The first carboranes, a novel class of polyhedral organoborane compounds, were discovered in the late 50's[1]. Although complete elucidation of their structures did not occur for several years, a number of derivatives received immediate attention for polymer synthesis. The impetus in this early phase of development stemmed from the search for high energy propellants, one of the two areas of potential application which served to promote carborane polymer research. The other and ultimately more important one was the quest for thermally stable polymers based on carborane nuclei as building blocks linked by strong bonds. The bulk of today's work is still directed toward high-temperature applications.

"PENDANT-CARBORANE" POLYMERS

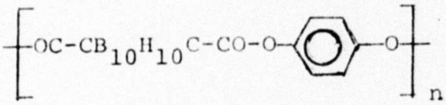
In this paper principal attention will be given to polymers with carborane moieties in the backbone as opposed to those having solely pendant carborane groups. Yet it was the synthesis of the latter type which was pursued at the outset, and the species mainly employed was o-carborane, one of the three icosahedral carborane isomers[2]. Thus, homopolymerization of 1-vinyl-o-carborane was, after much experimentation, finally achieved by use of phenyl lithium as catalyst[3], while aluminum chloride was found to polymerize 1-allyl-o-carborane and 1-isopropenyl-o-carborane; the vinyl and allyl derivatives copolymerize in the presence of peroxides. In addition to being appendages to polyalkylene chains, o-carborane moieties have also been attached to polysiloxanes via alkyl linkages, the method of synthesis being co-hydrolysis of dimethyldichlorosilane with an o-carboranylalkylmethyl dichlorosilane[4]. The polymers shown below will serve as examples for appending o-carborane moieties directly or indirectly to these chains.

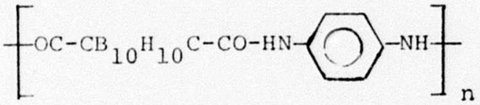




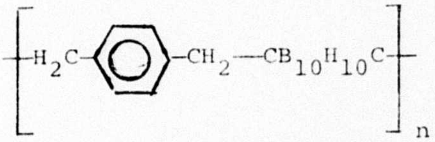
"BACKBONE-CARBORANE" POLYMERS WITH ORGANO-TYPE LINKAGES

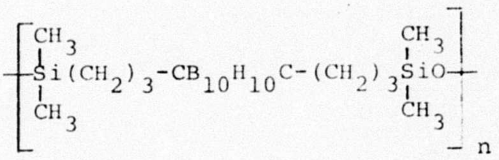
Most important, however, the bifunctionality of the carboranes due to their two strongly acidic and easily replaceable carbon-bond hydrogens permitted their inclusion in polymer chains. These can be divided into two general classes based on the character of the bonding between carborane moieties, namely, whether carbon-containing or carbon-free. Of the former organo type, condensation polymers such as polyesters, polyamides and polyurethanes have been obtained through conventional organic synthesis methods[5]; typical examples derived from m-carborane dicarboxylic acid dichloride and esters or amines are the following:





Polymers especially prepared to attain greater heat stability are exemplified below by a poly(p-xylene-m-carborane)[6] and a poly(alkylenesiloxane-m-carborane)[7].





$$\left[-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{Si}}}(\text{CH}_2)_3-\text{CB}_{10}\text{H}_{10}\text{C}-(\text{CH}_2)_3\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{Si}}}\text{O}-\right]_n$$

Of the polymers treated in these two sections, some exhibited enhanced thermal stability when compared with their non-carborane structural analogues. However, none showed sufficient improvement in thermal behavior to warrant in-depth exploitation.

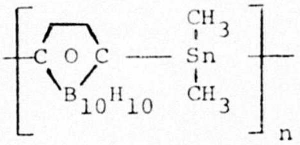
"BACKBONE-CARBORANE" POLYMERS WITH INORGANIC LINKAGES

In 1962, the Office of Naval Research started to sponsor a series of exploratory projects on boron cluster compounds. Our part in this program focussed on the utilization of specific clusters, especially carboranes, for building essentially inorganic polymers with superior heat stability; to this end, all efforts were confined to non-carbon linkages.[8]

A. Single-Atom-Bridged Carborane Chains

Of the several bonding systems examined, the connecting of carborane nuclei through single-atom bridges aroused interest, although in chronological order one of the later approaches. Polymers of this type were investigated independently by an Italian team and by us from 1966 on and representative species, as depicted below, are a mercury-[9], a sulfur-[10], as well as a tin-linked[11] polymer:

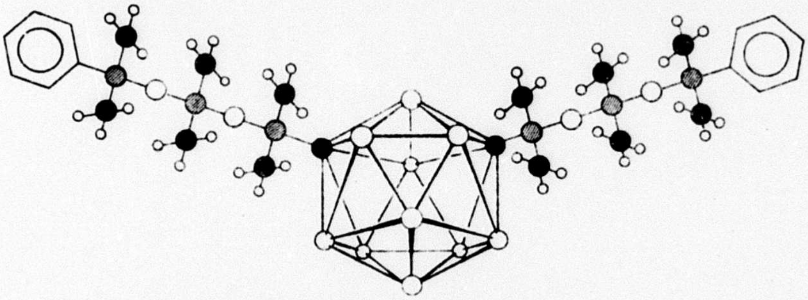
$$\left[-\text{CB}_{10}\text{H}_{10}\text{C-Hg}-\right]_n \qquad \left[-\text{CB}_{10}\text{H}_{10}\text{C-S}-\right]_n$$



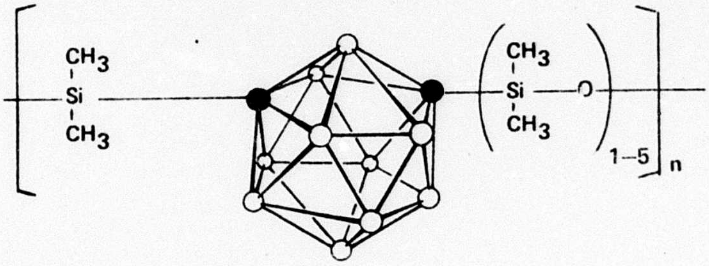
The most stable of these, poly(dimethyltin-p-carborane), softens around 420°C but undergoes exothermal decomposition at 425°C according to TGA and DTA measurements.

B. Poly(m-carboranylenesiloxanes)

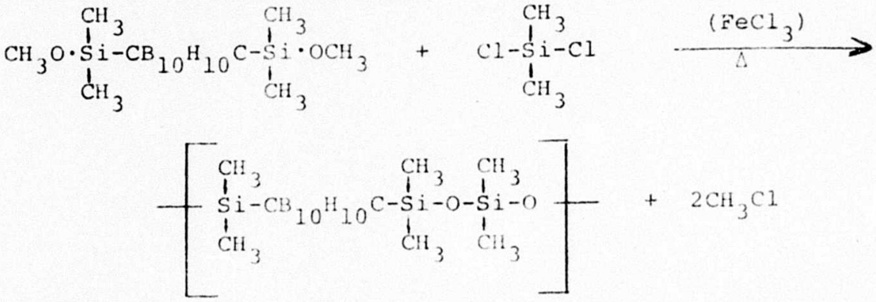
Our major effort concerned the attachment of siloxanyl groups to m-carborane nuclei which resulted in monomeric, oligomeric and polymeric species. As for the first category, bis(tri and tetrasiloxanyl)-m-carboranes proved to be, in general, mobile high boiling liquids. The combination of their low pour points, low ASTM viscosity slopes, high flash points and adequate wear characteristics has generated interest in their use as high-temperature lubricants. A typical representative is 1,7-bis-(5-phenylhexamethyltrisiloxanyl)-m-carborane[12]:



Principal attention, however, was given to the polymeric species having the following general formula:



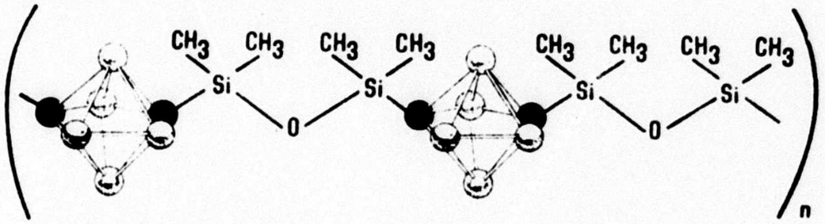
Their synthesis by ferric chloride-catalyzed copolymerization of bis(alkoxysilyl)-carboranes and dichlorosilanes was published in 1966[13] and is exemplified here by the DEXSIL 200 (SiB-2) representative.[14]



$$CH_3O\cdot\underset{CH_3}{\overset{CH_3}{Si}}-CB_{10}H_{10}C-\underset{CH_3}{\overset{CH_3}{Si}}\cdot OCH_3 \quad + \quad Cl-\underset{CH_3}{\overset{CH_3}{Si}}-Cl \quad \xrightarrow[\Delta]{(FeCl_3)}$$

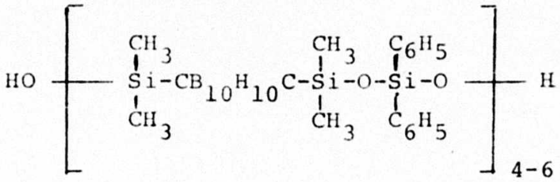
$$\left[-\underset{CH_3}{\overset{CH_3}{Si}}-CB_{10}H_{10}C-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\right] \quad + \quad 2CH_3Cl$$

The same method of synthesis was applied in 1970[15] to the preparation of analogous poly(carboranesiloxanes) containing the "smaller" C_2B_5 cages, either by themselves as depicted below (SiB-1 configuration) or in combination with C_2B_{10} nuclei.



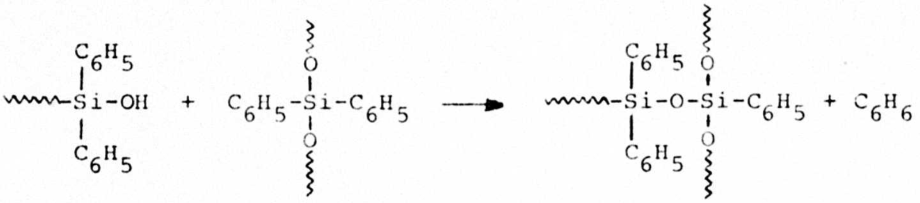
The aforementioned DEXSIL 200 species is obtained as a rubbery polymer and became the subject of a broad application program aimed at providing high-temperature elastomers. Evaluation data on compression-molded and peroxide-cured vulcanizates such as panels, O-rings and diaphragms in regard to weight loss, compression set, retention of tensile strength and elongation after heat-aging, demonstrated unprecedented stability in the 350° to 450°C range[16]. These results were corroborated by chemical stress-relaxation measurements up to 350°C[17]. However, consistent reproducibility of base stocks could not be achieved since the bulk polymerization employed involves uncontrollable crosslinking at the elevated temperatures (up to 185°C) required to complete the reaction.

The related DEXSIL 202 species, in which two methyl groups are replaced by phenyl groups, is a highly viscous liquid of low molecular weight having terminal OH groups.



$$HO-\left[\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{Si}}-CB_{10}H_{10}C-\underset{\substack{|\\CH_3}}{\overset{\substack{CH_3\\|}}{Si}}-O-\underset{\substack{|\\C_6H_5}}{\overset{\substack{C_6H_5\\|}}{Si}}-O\right]_{4-6}-H$$

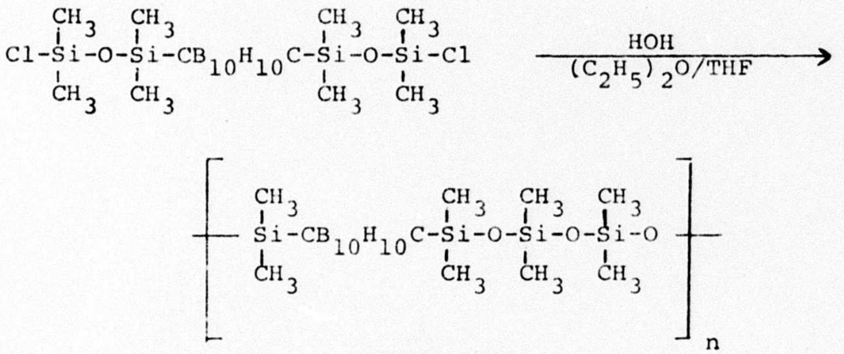
Simple heat-curing will result in cleavage of phenyl groups by acidic protons of the Si-OH moieties generating a network polymer based on Si-O-Si crosslinks[18].



$$\sim\underset{\substack{|\\C_6H_5}}{\overset{\substack{C_6H_5\\|}}{Si}}-OH + C_6H_5-\underset{\substack{|\\O\\\wr}}{\overset{\substack{\wr\\O\\|}}{Si}}-C_6H_5 \longrightarrow \sim\underset{\substack{|\\C_6H_5}}{\overset{\substack{C_6H_5\\|}}{Si}}-O-\underset{\substack{|\\O\\\wr}}{\overset{\substack{\wr\\O\\|}}{Si}}-C_6H_5 + C_6H_6$$

This chemical behavior permits its potential use for two applications; first, as a protective coating on a variety of substrates including metals, glass, and fabrics and second, as a rigid foam which can be cured in place. As for the latter, viscous DEXSIL 202 formulations are heated to 300°C to give products in the density range of 15 to 50 lbs/ft^3 having compressive strength between 500 and 2000 psi. No added blowing agent is needed since the benzene eliminated during crosslinking serves this function. Appropriately compounded foams are dimensionally stable at 400°C and even above. - Properties of 1-4 mil thick neat coatings on steel are >80 in·kg impact resistance, ~500g scrape adhesion, pencil hardness of H and good flexibility (~10% elongation). With appropriate fillers, thermostability at 300-400°C for several 100 hours is attained.

Our dissatisfaction with the practical aspects of the prematurely crosslinked DEXSIL 200 raw gum compelled us to look at synthetic approaches leading to strictly linear species. In 1970/71, these efforts culminated in a simple hydrolytic condensation reaction providing the desired representatives in the 300, 400, and 500 series.[19]



$$\mathrm{Cl{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}CB_{10}H_{10}C{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}Cl} \xrightarrow[(C_2H_5)_2O/THF]{HOH}$$

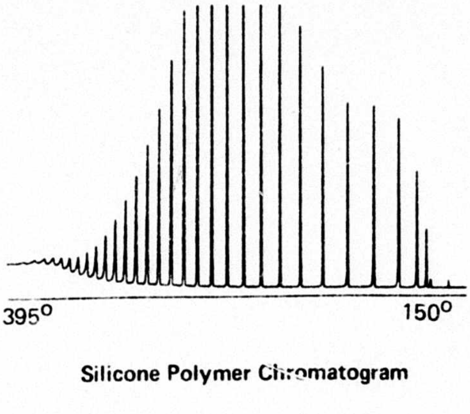
$$\left[\mathrm{\overset{CH_3}{\underset{CH_3}{Si}}{-}CB_{10}H_{10}C{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O{-}\overset{CH_3}{\underset{CH_3}{Si}}{-}O} \right]_n$$

DEXSIL 300

This method was not adaptable to the 200 series since the silicon atom attached directly to the carborane cage is reluctant to form siloxane linkages; instead, the respective silanol is formed.

Later in 1971, a second synthetic method for obtaining linear carboranesiloxanes became known[20] through work by ChemSystems, Inc. Instead of hydrolysis, it involves alcoholysis of bis-(chlorosilyl or siloxanyl)-carboranes. With "small" carboranes such as the C_2B_5 cage, it is applicable to the entire range of SiB polymers; in the C_2B_{10} class, only the SiB-1 (or DEXSIL 100) types are excluded. Copolymerization of chlorosilyl derivatives of both cage configurations provides random copolymers with promising thermal and oxidative stability.

To date, one of these linear polymers, DEXSIL 300, has proven to have wide utility, namely, as a high-temperature chromatographic phase[21]. It has extended the range of gas chromatography to 500°C now permitting analysis of high boiling liquids and polymers; a representative chromatogram showing the components of a silicone polymer is depicted.[22]



Silicone Polymer Chromatogram

Selected linear species of the DEXSIL 300 and 400 series can now be obtained having molecular weights >100,000. Optimum cross-linking systems for their conversion into suitable vulcanizates are under development. In addition, synthesis efforts are under way to improve fluid resistance and low-temperature properties.

ACKNOWLEDGMENT

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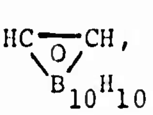
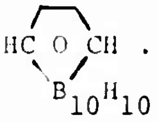


$HC{-}CH$, $B_{10}H_{10}$, $HCB_{10}H_{10}CH$,   and



$HC\ O\ CH$. $B_{10}H_{10}$

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