

CARBORANE POLYMERS

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ABSTRACT

The evolution of polymers incorporating the *closo*-carboranes $C_2B_5H_7$ and $C_2B_{10}H_{12}$ is reviewed. Both addition and condensation polymers and copolymers are described which include various examples of polyesters, polyvinyls and polyamides. Primary emphasis is placed upon the polycarboranesiloxane polymers which exhibit unparalleled thermal stability.

INTRODUCTION

At present the most promising use for the various carboranes is to incorporate them into polymers with the objective of building into the polymers special properties such as high temperature resistance and/or specialized chemical resistance. To date investigators have successfully incorporated carboranes both into the backbone of most of the common types of addition and condensation polymers and also in many cases as pendant groups or side chains. When they are incorporated into the backbone of silicone polymers the carboranes show particularly interesting properties. Olin's Dexsil polymers based upon $C_2B_{10}H_{12}$ are prime examples, and soon similar materials based upon the *closo*-carborane $C_2B_5H_7$ will be available.

One purpose of this lecture is to review in a cursory fashion examples of the numerous types of carborane polymers which have been prepared and thus serve as the background upon which the more recent polymer progress has been achieved.

Also, we will cover the budding field of $C_2B_5H_7$ -based polymers which are just now moving out of laboratory curiosity status and into commercial availability.

BACKGROUND

The field of carborane (including borane) chemistry may be divided into three parts, *closo*-carboranes, *nido*-carboranes, and *arachno*-carboranes (examples in Figure 1), which may be generalized as $C_{0-2}B_nH_{n+2}$, $C_{0-4}B_nH_{n+4}$ and $C_{0-6}B_nH_{n+6}$ with respect to their empirical formulae (Figure 2)¹. It should be noted that only those particularly stable species lacking any bridge hydrogens have been incorporated successfully into polymers with high thermal stabilities. Bi-functionality is also important, hence $C_2B_{10}H_{12}$, $C_2B_8H_{10}$ and $C_2B_5H_7$ (no bridge hydrogens and bi-functional) have been successfully utilized while the *closo*-carborane CB_5H_7 (unstable as it contains one bridge hydrogen) has only limited prospects as a polymer precursor. We suggest strongly that the presumed great stability

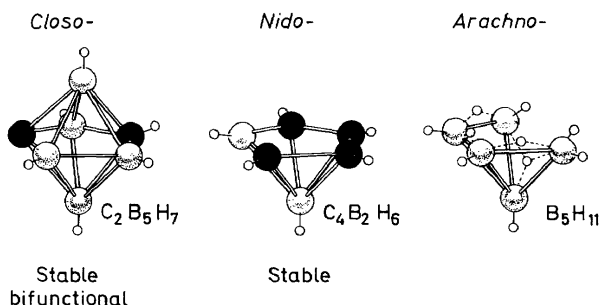


Figure 1. Examples of the three carborane classes.

of the closed-cage *closo*-carboranes is over-rated and that open-caged *nido*-carboranes such as $C_4B_2H_6$, $C_4B_6H_{10}$ and $C_4B_9H_{11}$ (containing four carbons but no bridge hydrogens) will be as stable, or in some cases more stable, than the related *closo*-carboranes; however, it may be difficult to obtain bi-functional derivatives to make them suitable as polymer precursors.

The following examples will serve to illustrate the richness and diversity of ways in which $C_2B_{10}H_{12}$ carborane isomers can be incorporated into polymers. Three excellent reviews written by Heying², Schroeder³ and Korshak *et al.*⁴ have appeared and are recommended to the reader for a more complete description. Selected examples are depicted in the following figures.

Vinyl-1,2- $C_2B_{10}H_{11}$ has been made into a polymer by Heying *et al.*⁵, (Figure 3) as has allyl-1,2- $C_2B_{10}H_{11}$ ⁶. Green and co-workers produced polymers of isopropenyl-1,2- $C_2B_{10}H_{11}$, the first derivative of $C_2B_{10}H_{12}$ to be discovered⁷. Copolymers of vinyl-1,2- $C_2B_{10}H_{11}$ and butadiene have been prepared by Clark *et al.*⁸ (Figure 4). A methacrylate polymer has also been produced⁷. Numerous polyesters typified by Heying's polymer⁹ as shown in Figure 5 have been prepared and polyamides (Figure 6) have been prepared by Korshak *et al.*¹⁰. Polyurethanes, where the —NCO group is both adjacent to the 1,2-carborane (Heying *et al.*¹¹) and in a more remote location (Akimov *et al.*¹²), have been prepared.

Green *et al.*¹³ prepared the first carborane-siloxane polymers (Figure 7) which utilized a number of methylene groups to separate the 1,2- $C_2B_{10}H_{11}$ -moiety from the silicone chain. Papetti *et al.*¹⁴ found that the bis-dihydroxy derivatives of two of the $C_2B_{10}H_{12}$ isomers formed either exocycles or dihydroxy derivatives but not polymers (Figure 8). These workers utilized $FeCl_3$ and elevated temperatures¹⁵ (Figure 9) to produce the desired polymers. This slowness in reactivity is in contrast to the behaviour of the $C_2B_5H_7$ derived analogue where the polymer is formed spontaneously upon hydrolysis at room temperature.

Similar syntheses produced SiB-2, -3, and -4 (now called Dexsils 200, 300 and 400) where 2, 3 or 4 stands for the number of oxygens between the carborane moieties (Figure 10).

Many other polymers incorporating 1,7- $C_2B_{10}H_{12}$ groups in the backbone have been prepared and have been reviewed by Heying², Schroeder³, and

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Closso-		Nido-		Arachno-	
Carboranes	Boranes	Carboranes	Boranes	Carboranes	Boranes
4					
5	$C_2B_3H_5$		B_3H_9		B_4H_{10}
6	$C_2B_4H_6$ [$C_1B_5H_6^-$] $B_6H_6^{2-}$	$C_4B_2H_6$ $C_3B_3H_7$ $C_2B_4H_7^-$	$B_5H_8^-$ $C_1B_5H_9$ B_6H_{10}		B_5H_{11}
7	$C_2B_5H_7$ $B_7H_7^{2-}$				B_6H_{12}
8	$C_2B_6H_8$ $B_8H_8^{2-}$		B_8H_{12}		
9	$C_2B_7H_9$ $B_9H_9^-$			$C_2B_7H_{13}$ $C_{10}B_{11}H_{13}$	B_9H_{14}
10	$C_2B_8H_{10}$ $C_1B_9H_{10}^-$ $B_{10}H_{10}^{2-}$ [$B_{10}H_{11}^-$]	$[C_4B_6H_{10}] [C_3B_7H_{11}] [C_2B_8H_{12}]$ B_9H_{12} $B_{10}H_{13}$ $B_{10}H_{12}^{2-}$	$B_{10}H_{14}$	$[C_2B_8H_{14}]$ $B_{10}H_{12}^{2-}$ $B_{10}H_{15}^-$	B_9H_{15}
11	$C_2B_9H_{11}$ $C_1B_{10}H_{11}^-$ $B_{11}H_{11}^{2-}$	$C_2B_9H_{12}$ $C_2B_9H_{11}^{2-}$ $C_1B_{10}H_{11}^{3-}$	$B_{11}H_{15}$ $C_1B_9H_{13}$ $B_{11}H_{14}$ $B_{11}H_{13}^{2-}$		
12	$C_{12}B_{10}H_{12}$ $C_1B_{11}H_{12}^-$ $B_{12}H_{12}^{2-}$				
C_2	C_1	C_4	C_3	C_2	C_1
	B_nH_{n+2}	$C_{0-2}B_nH_{n+2}$	B_nH_{n+4}	$C_{0-4}B_nH_{n+4}$	B_nH_{n+6}

Figure 2. 'Map' of the carboranes.

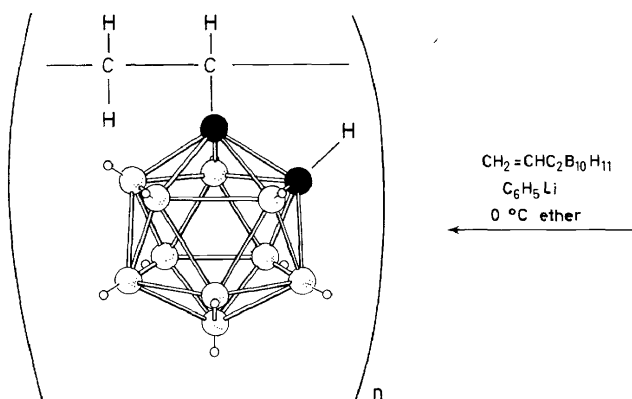


Figure 3. Vinylcarborane polymer. Mol. wt 50 000–140 000, Softened at 250–280°C, soluble in ether or benzene, insoluble in aliphatic hydrocarbons.

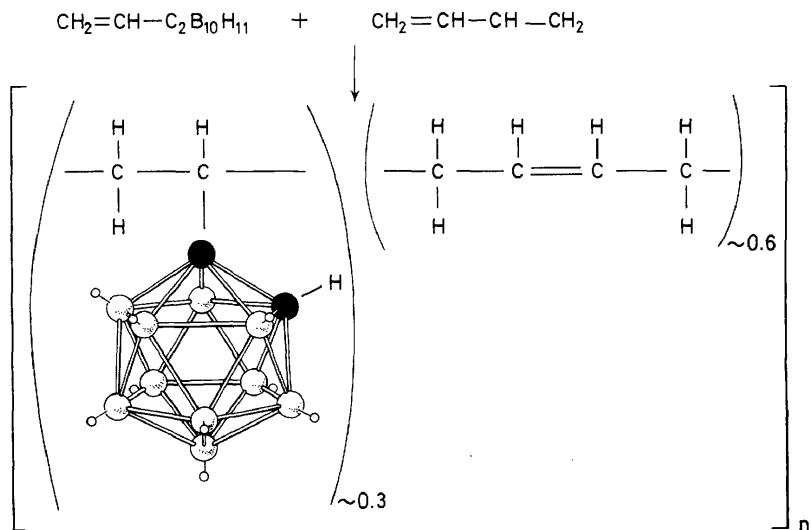


Figure 4. Copolymer of vinylcarborane and butadiene. High molecular weight rubbers, sulphur crosslinking.

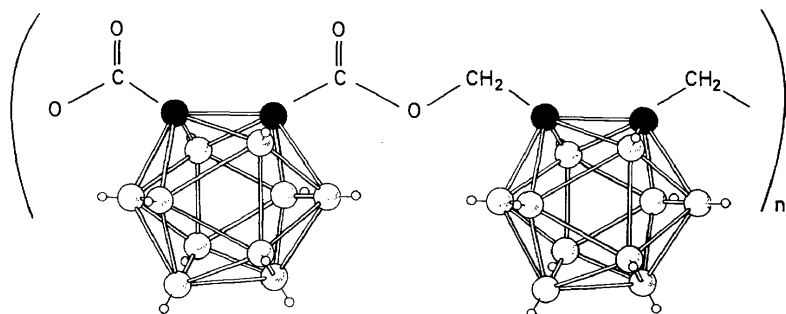
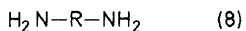
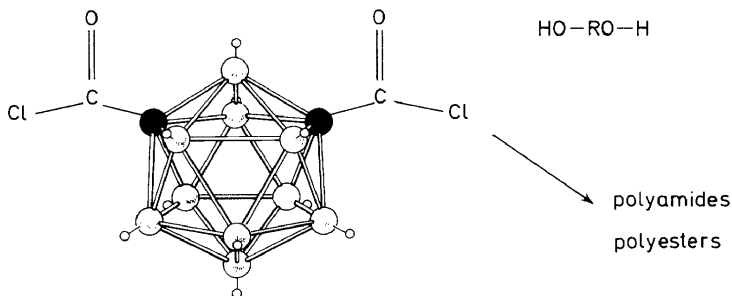
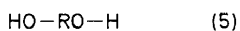


Figure 5. Carborane polyester.

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R = alkyl or aryl



Chemically resistant

Figure 6. Carborane polyesters and polyamides.

Korshak *et al.*⁴. These polymers utilize $\text{>Sn(CH}_3)_2$, $\text{>Sn(C}_6\text{H}_5)_2$, $\text{>Ge(CH}_3)_2$, $(-\text{Ge(CH}_3)_2)_2\text{NH}$, >S , >S=O , >C=O , >P-Cl , P-OCH_3 groups as connective units between the carbons of the 1,7- $\text{C}_2\text{B}_{10}\text{H}_{10}$ units. Schroeder's review in particular covers Dexsil 201 and Dexsil 202 which are remarkable polymers and have become commercial items as coatings (201) and rigid foams (202).

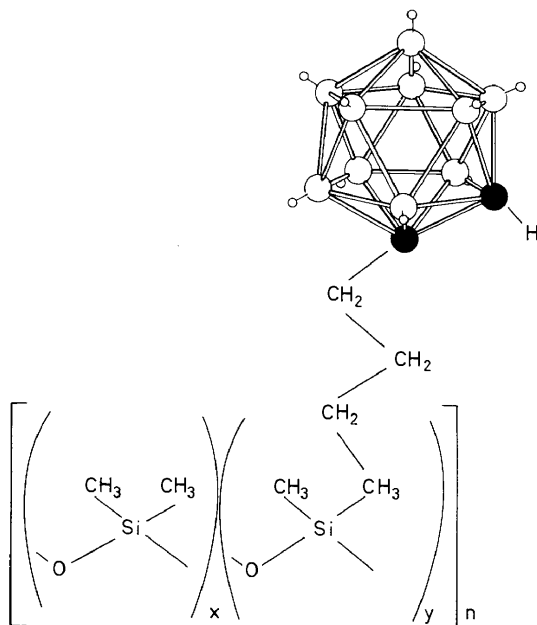


Figure 7. First carborane-siloxane polymers. Mol. wt. $\sim 13\,000$.

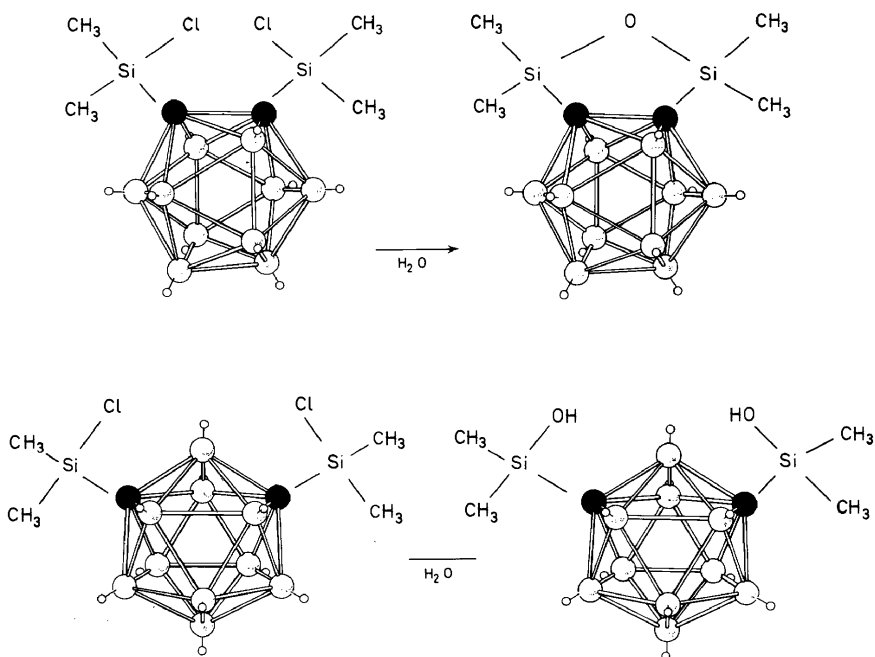


Figure 8. Hydrolysis of bis-dichlorosilyl derivatives of $C_2B_{10}H_{12}$.

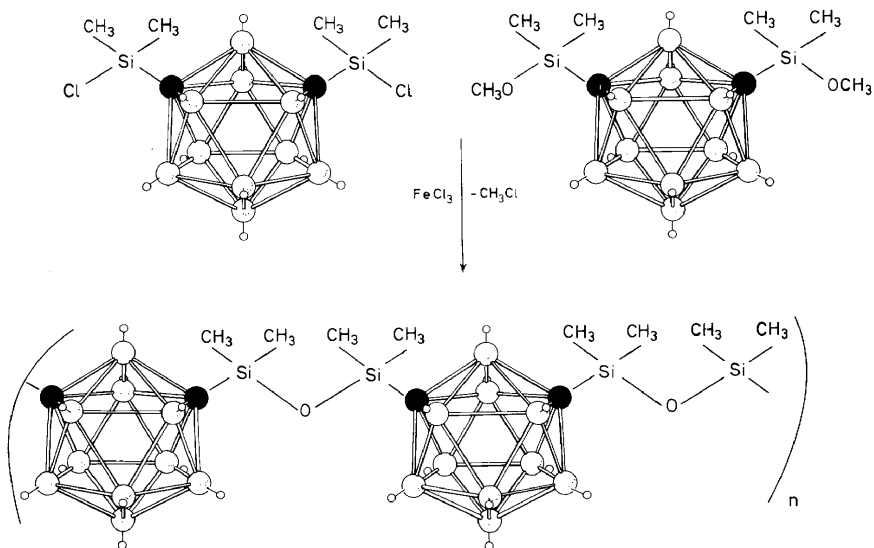


Figure 9. $FeCl_3$ catalysed polymerization. 10-SiB-1 crystalline at room temperature, softens at $\sim 24.5^\circ C$.

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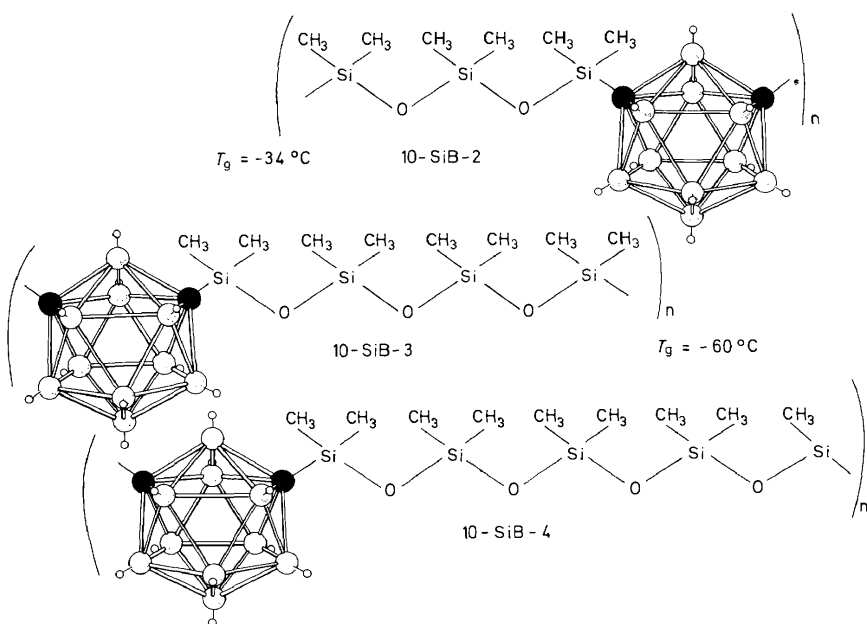


Figure 10. SiB/Dexsil polymers.

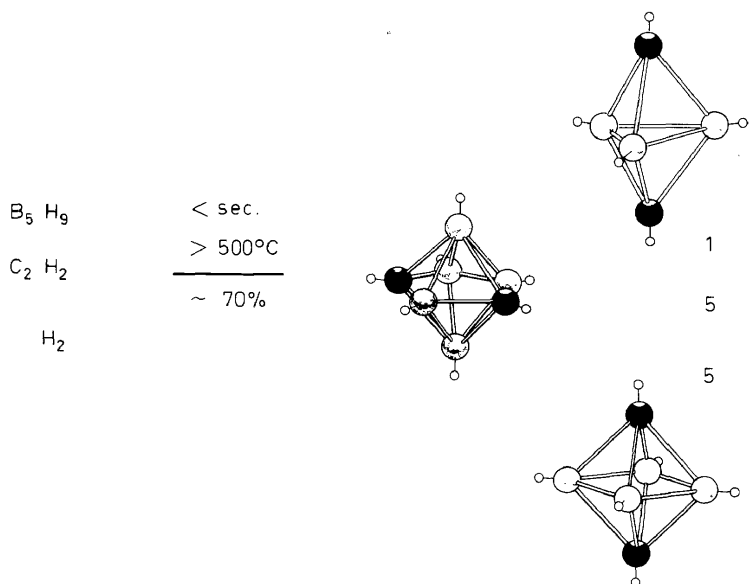


Figure 11. Direct synthesis of carboranes (1964–1967).

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It was against this fertile background of the successful production of many types and kinds of polymers based upon 1,2-C₂B₁₀H₁₂ and 1,7-C₂B₁₀H₁₂ chemistry that we were sponsored in 1964 to make similar polymers (i.e. carborane-siloxanes from 2,4-C₂B₅H₇, 1,6-C₂B₄H₆ or 1,5-C₂B₃H₅). At that time, however, the known syntheses produced only trace amounts of these carboranes and for the next four years (1964-1967 inclusive) we searched and finally found a good synthesis (*Figure 11*). During 1965 we determined, by using trace amounts (a few grams) of C₂B₅H₇, that the dilithio derivative, Li₂C₂B₅H₇, and the silyl derivatives (e.g. ClSi(CH₃)₂)₂C₂B₅H₇) could be produced. We were thus assured that polymers could be produced if we did indeed successfully devise a method of producing the smaller carboranes in larger quantities.

Our direct synthesis¹⁶ of the smaller carboranes from the reaction of C₂H₂, H₂ and B₅H₉ produces a number of byproducts in addition to the smaller carboranes C₂B₃H₅, C₂B₄H₆ and C₂B₅H₇. The byproducts are, however, *B*-methyl derivatives of the smaller carboranes so that all of the compounds retain their two CH groups, assuring bi-functionality and non-interference in the subsequent production of the polymers. *Figure 12* shows

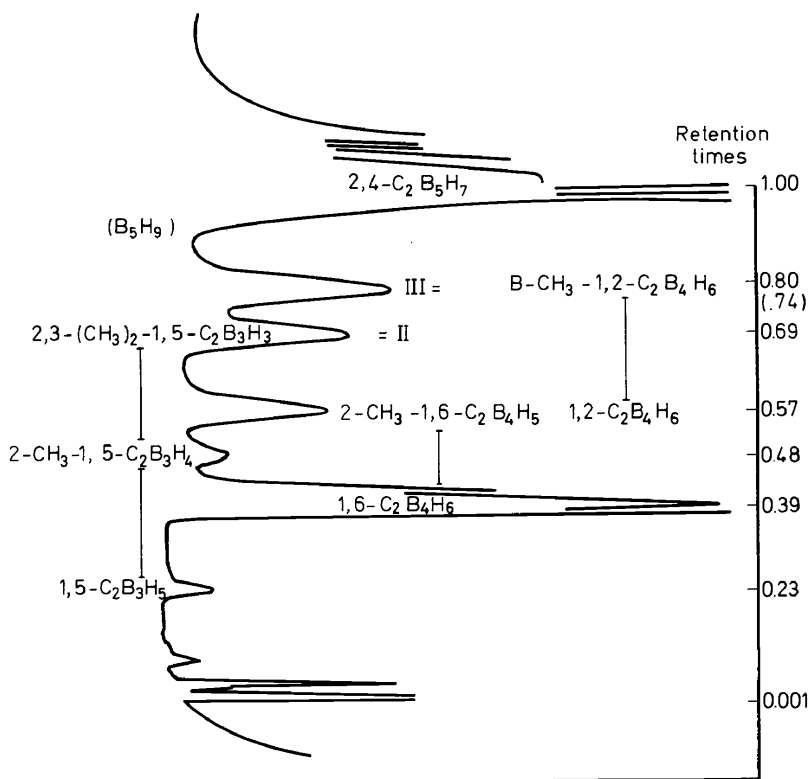


Figure 12. Gas-liquid chromatogram of lower molecular weight *closo*-carboranes from pyrolysis of acetylene and pentaborane.

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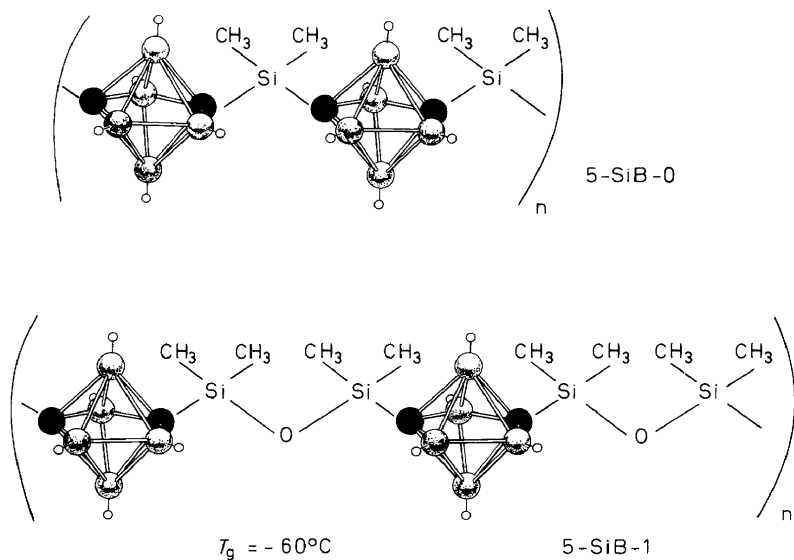


Figure 13. 5-SiB-0 and 5-SiB-1 polymers.

the separation of the less volatile fraction of a typical preparation.

5-SiB-0, 5-SiB-1 and 5-SiB-2 polymers (Figures 13–15), including 5-SiB-1 polymers modified with 5–20 per cent $\text{C}_2\text{B}_{10}\text{H}_{12}$ or $\text{C}_2\text{B}_8\text{H}_{10}$ substituted for $\text{C}_2\text{B}_5\text{H}_7$, were prepared utilizing standard synthetic techniques (FeCl_3 and a temperature of 180°C) pioneered by Olin. The 5-SiB-2 was a rubber,

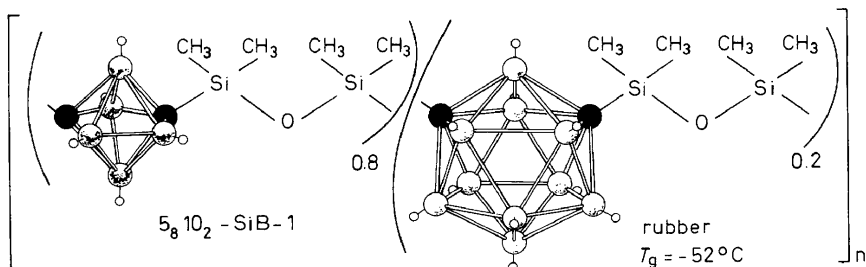
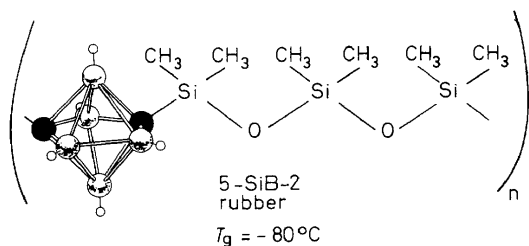


Figure 14. 5-SiB-2 and modified $5_8 10_2$ -SiB-1 polymers.

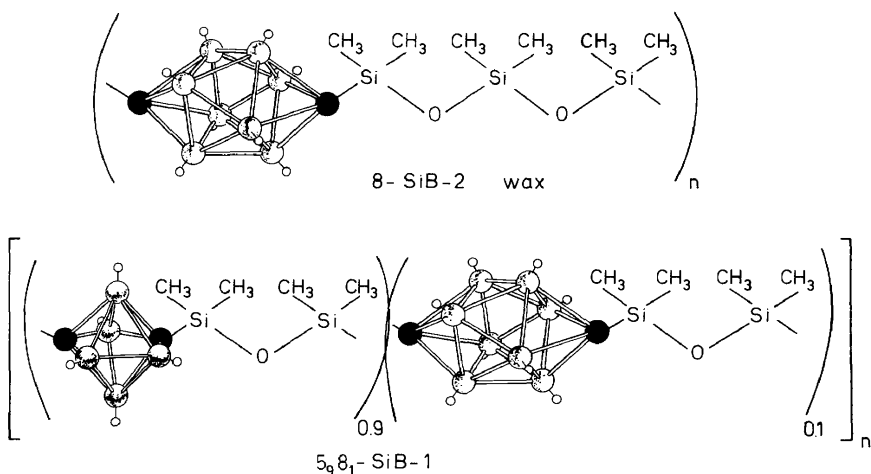
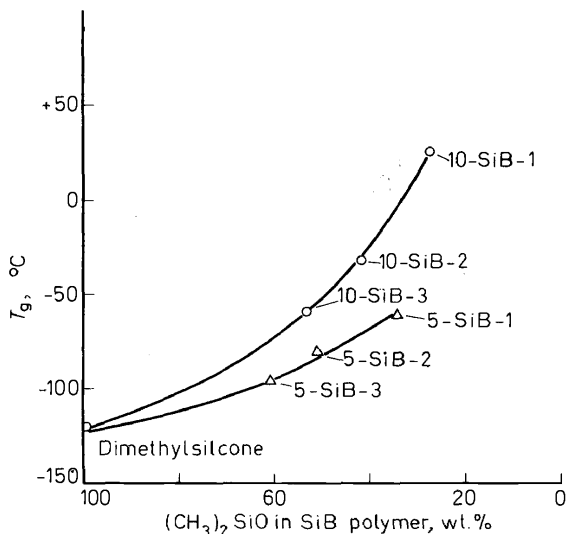


Figure 15. Modified polymers of 5-SiB-1 and 5-SiB-2.

however, and the incorporation of small amounts of the $C_2B_8H_{10}$ or $C_2B_{10}H_{12}$ carboranes was later found necessary to break up the crystallinity of the 5-SiB-1 polymer when an elastomeric product was desired. Kesting *et al.*¹⁷⁻¹⁹ cover these areas in detail in a continuing series of articles in the *Journal of Applied Polymer Science*. Figures 16 and 17 show the relative effects of the various SiB structures and the glass transition temperatures, a low value being a prerequisite for elastomer production.

We have recently found a superior polymer¹⁹ and/or prepolymer preparation (Figures 18, 19) of the carborane-siloxane polymers. While $(ClSi(CH_3)_2)_2-$

Figure 16. Effect of dimethylsiloxane concentration in carborane-siloxane polymers upon T_g .

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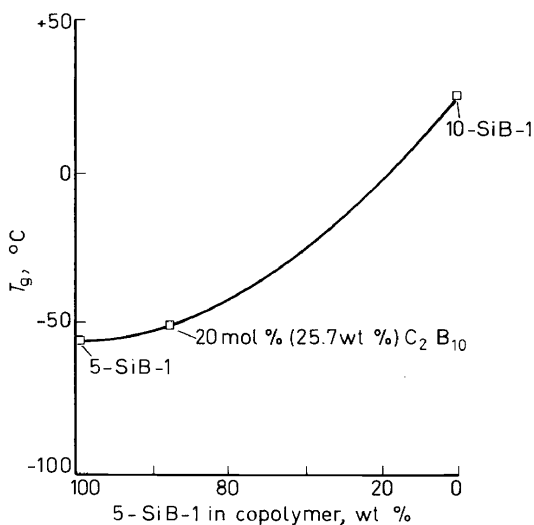


Figure 17. Effect of 5- and 10-SiB-1 copolymer composition upon T_g .

$C_2B_5H_5$ was being converted into $(CH_3OSi(CH_3)_2)_2C_2B_5H_5$ it was discovered by Newman of our laboratory that the 5-SiB-polymer was being prepared directly, accompanied by slight alcoholysis of the carborane cage as revealed by B—O absorption in the i.r. spectrum. Further experimentation revealed that the related $C_2B_{10}H_{12}$ derivative would not form a polymer in like fashion, confirming Olin's experience. In addition, we found that the $C_2B_{10}H_{10}(Si(CH_3)_2Cl)_2$ degraded more rapidly than its C_2B_5 analogue in the alcohol (methanol). To circumvent this difficulty, as the $C_2B_{10}H_{10}$

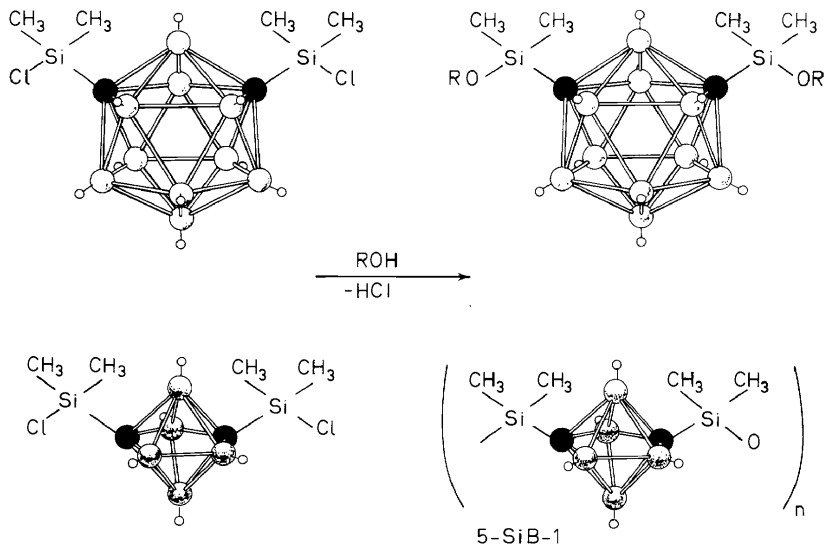


Figure 18. Polymerization by alcoholysis.

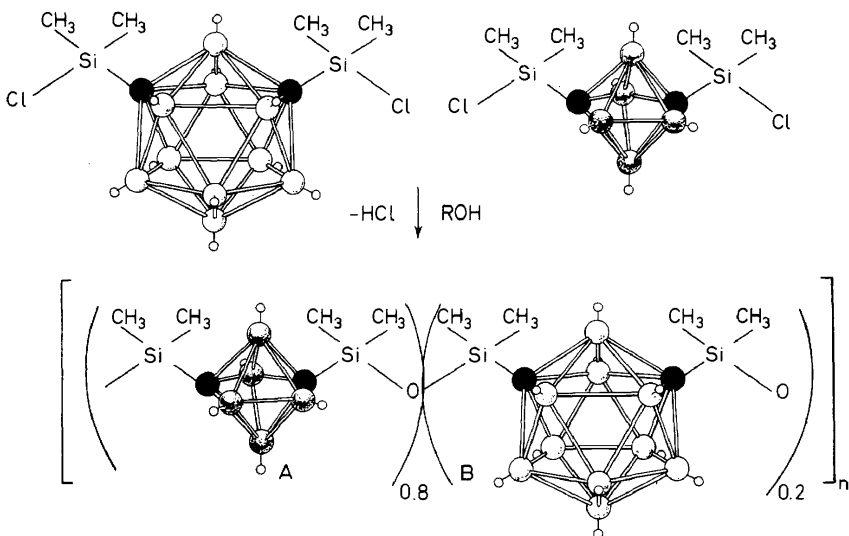
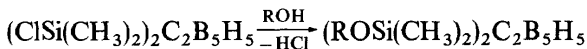


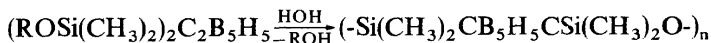
Figure 19. Modified 5-SiB-1 polymers by alcoholysis.

moiety was needed to break up crystallinity, we tested a number of common alcohols and found as expected that the tertiary alcohols accelerated the polymerization and simultaneously produced less degradation of the $\text{C}_2\text{B}_{10}\text{H}_{10}$ and $\text{C}_2\text{B}_5\text{H}_5$ cages. Since the 5-SiB-1 monomer either alone or in admixture with the 10-SiB-1 monomer will form polymers (incorporating $\text{C}_2\text{B}_{10}\text{H}_{10}$ moieties when they are present) there is, we believe, little chance that $\text{C}_2\text{B}_{10}\text{H}_{10}$ moieties are adjacent in the resulting polymer, thus assuring maximum effectiveness of the $\text{C}_2\text{B}_{10}\text{H}_{10}$ moieties in breaking up crystallinity.

Since it is known that the alcoholysis produces the alkoxy derivative very rapidly



and that the HCl and ROH should react slowly to produce RCl and [HOH] (most facile with tertiary alcohols), the mechanism may be simply the slow homogeneous generation of nascent water which promotes polymerization whilst simultaneously regenerating the alcohol.



In an acid medium the H_2O may exist as H_3O^+ rather than H_2O and is thus less likely to attack the BH groups. We found that the addition of a small amount of concentrated sulphuric acid also retards alcoholysis or hydrolysis of the BH groups.

The 5-SiB-1 polymers lose 10–12 weight per cent at about 375° to 400°C in argon in contrast to an apparent ~ 0 per cent loss in air which suggests that

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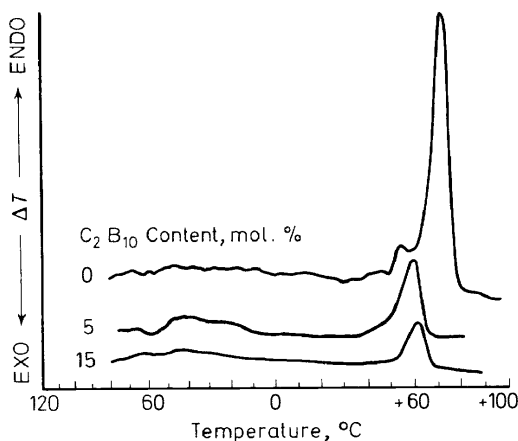


Figure 20. DSC tracings for C_2B_{10} -modified C_2B_5 -SiB-1 elastomers.

in the latter case oxygen pick-up balances weight loss. DSC spectra of the modified 5-SiB-1 polymers show the effects of chain disruptor percentage (Figure 20) and ageing (Figure 21) upon the crystallinity of the polymers. Figure 22 shows the effect¹⁸ of curing and modification upon the hardness of -SiB-1 polymers as they age at room temperature following melting and quenching. Figure 23 reveals the effects of crosslinking caused by radiation upon the polymer.

Without going into detail, since these results have not yet been published, Professor Gillham of Princeton has studied several of our 5-SiB-1 polymers by means of his Torsional Braid Analysis (TBA) technique (utilizing a torsional pendulum) and has been able to obtain what he terms thermo-

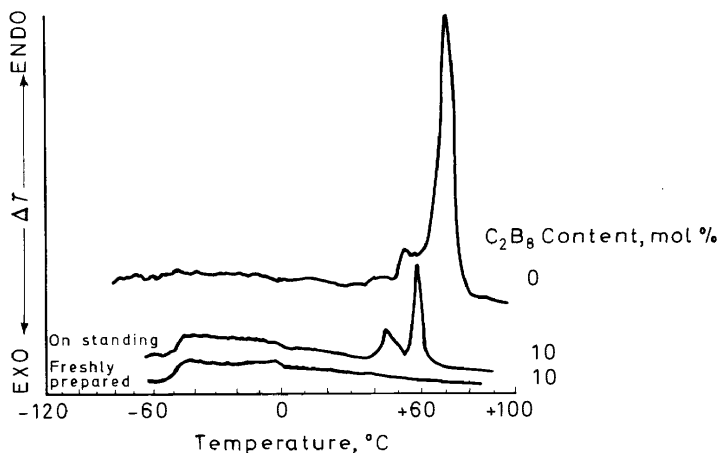


Figure 21. DSC tracings for C_2B_8 -modified C_2B_5 -SiB-1 elastomers.

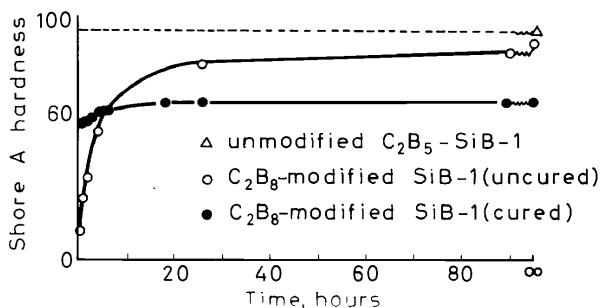


Figure 22. Shore A hardness versus time for $C_2B_5-SiB-1$ carborane-siloxane polymers.

mechanical spectra of both our modified and unmodified polymers. His method allows temperature rigidity and temperature/mechanical damping profiles to be obtained simultaneously with very small polymer samples. In contrast to other techniques it also pinpoints the temperatures at which glass and secondary transitions, crosslinking, etc., occur. Gillham's technique is an exceptionally powerful tool which we predict will find increasing utility in the characterization of newly discovered polymers, in many cases first prepared in minute quantities.

Some of our 5-SiB-1 polymers are undergoing tests as the liquid phase in various gas chromatographic applications. Within the last year or so, the Dexsil-300-GC polymers of Olin have found broad utilization in GLC applications at high temperatures. Our analogous 5-SiB-1 polymers currently crosslink some $40^\circ C$ below the Dexsil 300 (10-SiB-3) materials; however, our 5-SiB-1 polymers have produced columns with higher separating efficiencies (more theoretical plates per unit length) than has ever been observed with other materials. Moreover, after controlled crosslinking at $\sim 400^\circ C$ there is much less column bleed (as detected by flame ionization) at temperatures below $375^\circ C$ than has hitherto been observed with any other liquid phase.

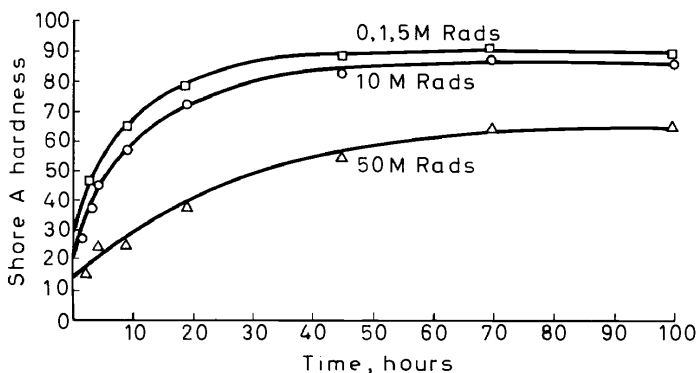


Figure 23. Shore A hardness versus time and β (3 MeV) dose for a 5-SiB-1 polymer containing 15 mol. % $m-C_2B_{10}$.

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