

Heat-Resistant Polymers Containing the Low Molecular Weight *closo*-Carboranes. III. The Preparation of Polycarboranesiloxane Polymers by Alcoholysis

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Synopsis

A new synthesis for carboranesiloxane polymers has been discovered. It involves the alcoholysis of the bischlorodimethylsilylcarborane monomers and the generation of the HCl catalyst in situ. Alcoholysis is applicable to the synthesis of most carboranesiloxane polymers, with the probable exception of the SiB-1 homopolymers of the larger carboranes. The attack of the B—H moieties in the carborane cage can be minimized both by the utilization of a tertiary alcohol and by the addition of excess acid when a primary alcohol is employed.

INTRODUCTION

Crystalline carboranesiloxane polymers of the 5-SiB-1 type,



prepared by the FeCl₃-catalyzed bulk condensation of the chloro- (i.e., ClSiR₂CB₅H₅CSiR₂Cl) and the methoxy- (i.e., CH₃OSiR₂CB₅H₅CSiOCH₃) monomers, have been reported.^{1,2} Amorphous copolymers, made by the incorporation of small quantities of larger carborane (—CB₈H₈C— or *m*-CB₁₀H₁₀C—) into the predominantly —CB₅H₅C— siloxane backbone have also been prepared.^{3,4} The 5-SiB-1 polymers, therefore, encompass a wide range of materials bounded at one extreme by homopolymer waxes and on the other by copolymer elastomers. These polymers are of considerable interest because of their high thermal and oxidative stability.⁵ Simplified routes to replace the high temperature and vacuum syntheses hitherto employed are currently being investigated. The present paper describes a study initiated in December 1970 which appears to be applicable to the preparation of all carboranesiloxane polymers with the probable exception of the SiB-1 homopolymers of the large carboranes. It is a simple alcoholysis procedure which employs ambient temperatures, atmospheric pressure, and a catalyst generated in situ.

EXPERIMENTAL

Polymer Synthesis

The new synthesis involves the addition of an alcohol to the 5-chloro monomer (i.e., 2,4-bis(chlorodimethylsilyl)-2,4-dicarba-*closo*-heptaborane-7) or mixtures thereof with the *m*-10-chloro monomer (i.e., 1,10-bis(chlorodimethylsilyl)-1,10-dicarba-*closo*-decaborane-10). In a typical example, 100 millimoles of 5-chloro monomer were placed in a flask to which 50 ml of an anhydrous alcohol was added. In another example, 50 ml of an alcohol was added to a flask containing 80 millimoles of 5-chloro monomer and 20 millimoles of the *m*-10-chloro monomer. After standing for periods varying between 20 and 200 hr, the precipitated polymers were extracted with solvent, precipitated, washed with water, and dried in a vacuum oven. This synthesis should be generally applicable to the preparation of SiB-1 polymers from the other small carboranes. The higher SiB polymers (i.e., SiB-2, -3, etc.) of C₂B₅ and C₂B₁₀, and most intermediate *closo*-carboranes (with the possible exception of C₂B₉H₁₁) are also accessible by this technique.

Analysis

Number-average molecular weights \bar{M}_n were determined in chloroform utilizing a vapor pressure osmometer (Mechrolab Model 201A). They are accurate to $\pm 10\%$. Melting point ranges were determined on a Fischer-Johns melting point apparatus. Infrared analyses were obtained utilizing a Perkin Elmer Model 21 spectrophotometer.

RESULTS AND DISCUSSION

During the course of the methanolysis^{1,2} of a large amount of 5-chloro monomer to produce 5-methoxy monomer, it was noticed by one of us (J.M.N.) that a white solid precipitate formed in the methanol phase after standing for several days. This precipitate was subsequently shown to be a partially soluble linear polymer whose infrared spectrum exhibited absorption (not present in the case of the 5-SiB-1 homopolymer prepared by anhydrous FeCl₃-catalyzed condensation) in the 7.2–7.9 μm range (maximum at 7.63 μm). This absorption is attributable to B—O stretching from B—O—R groups. The latter are the result of the alcoholysis of the B—H groups in the carborane cage.

A study was then made of the effects of the nature and concentration of the R radical in ROH upon polymer properties (Table I). Where R is H or a primary or secondary alkyl group, the B—H moieties in the carborane cage are attacked after standing for several days at ambient temperature to an extent sufficient to cause a substantial amount of B—OR group formation (polymers 1 to 6). Attack of the carborane cage is most severe when water and methanol are employed (polymers 1 and 2). The polymers produced in these cases were also found to be covalently crosslinked and

TABLE I
Properties of 5-SiB-1 Polymers Prepared by Alcoholysis^a

Polymer no.	Alcohol		Polymer property ^a					
	Species	Class	Concentration, <i>n</i> ROH/ <i>n</i> monomer	Physical appearance	Melting point range, °C	Magnitude of B—O stretching ^b	\bar{M}_n	DP
1	Water		11.1	White rubbery solid	54 to 180	s	1630	7.5
2	Methanol	1°	12.4	clear rubbery solid	74 to 180	s	995	4.6
3	1-Propanol	1°	6.67	white solid	24 to 35	s	1020	4.7
4	2-Propanol	2°	6.54	sl. yellow solid	-10 to -5	s	1080	5.0
5	Isoamyl	1°	4.6	colorless liquid	-15 to -10	s	515	1-2
6	Cyclohexanol	2°	5.28	sl. yellow liquid	30 to 40	s	620	2.0
7	Ethanol	1°	8.53	sl. yellow solid	58 to 69	m	2200	10.0
8	Methanol + H ₂ SO ₄ (10 ml)	1°	12.4	sl. yellow solid	68 to 72	m	2340	11.0
9	<i>t</i> -Amyl	3°	5.67	white solid	69 to 72	m	2625	12.0
10	<i>t</i> -Butyl	3°	5.33	white solid	65 to 71	w	2180	10.0
11	<i>t</i> -Amyl	3°	1.0	white solid	58 to 66	w	2325	11.0
12	<i>t</i> -Amyl	3°	2.0	white solid	61 to 72	w	2732	12.6
13	<i>t</i> -Amyl	3°	3.4	white solid	70 to 73	w	2712	12.5
14	<i>t</i> -Amyl	3°	5.67	white solid	35 to 48	w	1760	8.0

^a Polymers 1 to 13 inclusive are 5-SiB-1 homopolymers; polymer 14 is a SiB-1 copolymer containing 80 mole-% C₂B₅ and 20 mole-% C₂B₁₀.

^b s = Strong; m = medium; w = weak.

are encountered at the apex of two relatively small angles *within the cage*: a wide angle of 108° and a narrow angle of 63° . In both cases a large exterior angle results which can be expected to contribute to flexibility in the C—Si bond. Both carbon atoms in the $m\text{-C}_2\text{B}_{10}$ chloro monomer, on the other hand, are situated at the apex of *wide internal angles* of 124.5° , with the result that the exterior angle is much smaller and hence the C—Si bond more restricted than is the case for the 5-SiB polymers. This suggests that two $m\text{-C}_2\text{B}_{10}$ moieties cannot be made to adjoin one another in a SiB-1

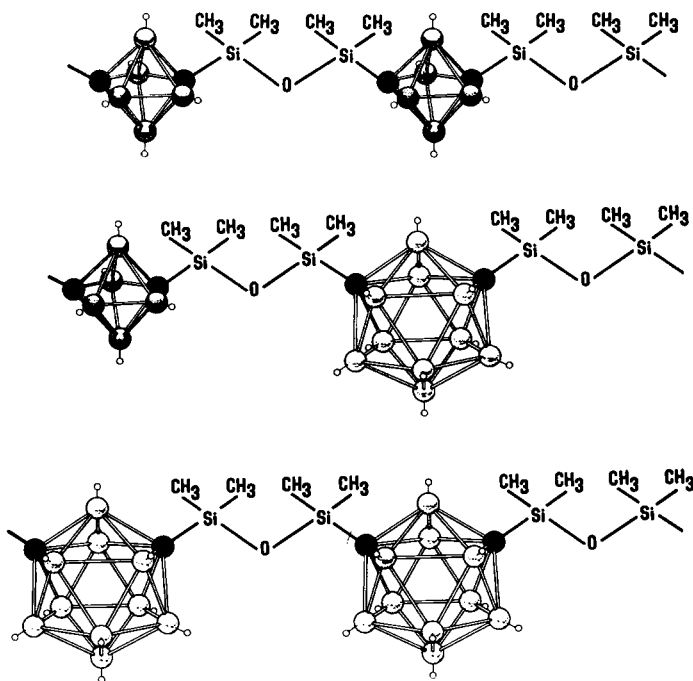


Fig. 1. Polycarboranesiloxane polymers of the SiB-1 type.

polymer unless forcing conditions are employed. Copolymers incorporating both C_2B_5 and C_2B_{10} monomers apparently represent a situation intermediate between 5-SiB-1 and 10-SiB-1 homopolymers, since the MW of the polymer containing 20 mole-% $m\text{-C}_2\text{B}_{10}$ (polymer 14) is lower than that of the 5-SiB-1 homopolymer and higher than that of the 10-SiB-1 homopolymer, which does not appear to form under the present set of conditions. In other words, a $m\text{-C}_2\text{B}_{10}$ monomer can be joined to a C_2B_5 monomer, but less readily than one C_2B_5 monomer to another of its own kind. This situation contributes to isolation of C_2B_{10} monomers which in turn acts to maximize randomness and hence elastomeric behavior on the copolymer.

Although low molecular weight polymers are obtained by alcoholysis, it is obvious that, where high molecular weight is desired, further polymerization can be effected by other techniques.

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