

High-Temperature Elastomers: A Systematic Series of Linear Poly(Carborane-Siloxane)s Containing Icosahedral ($-\text{CB}_{10}\text{H}_{10}\text{C}-$) Cages.

III. Spectroscopic Identification

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Synopsis

Documentation and preliminary analysis of the infrared and proton nuclear magnetic resonance spectra of a systematic series of poly(carborane-siloxane)s containing $-\text{CB}_{10}\text{H}_{10}\text{C}-$ cages are reported. Inconsistencies in the spectra are interpreted in terms of complications in the syntheses.

INTRODUCTION

Research in the field of high-temperature elastomers has led to the development of carborane-siloxane polymers which have elastomeric properties throughout the temperature range -100°C to $+500^{\circ}\text{C}$. The thermomechanical behavior of the linear poly(carborane-siloxane)s which form the basis of the present report have recently been investigated in order to relate their physical transitions,¹⁻³ and thermal¹ and oxidative⁴ stabilities at high temperature, to molecular structure. Such correlations depend on the correct assignment of structure which is usually made with spectral evidence. Inconsistencies often bear on complications in synthesis.

This communication presents documentation and preliminary analyses of the infrared spectra of the polymer films and of the high-resolution proton magnetic resonance spectra of the methyl-, 1,1,1-trifluoropropyl- and phenyl-silyl groups of the polymers in solution. Inconsistencies in the spectra are interpreted in terms of complications in the syntheses.

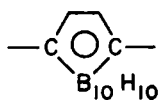
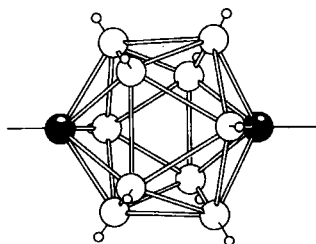
EXPERIMENTAL

Materials

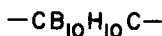
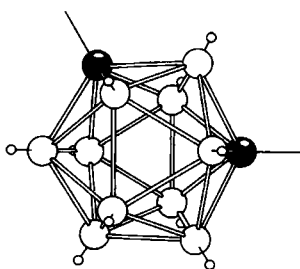
The polymers which are discussed in this report were synthesized, characterized, and supplied by the Olin Corporation Research Center,

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New Haven, Connecticut.⁵⁻⁷ The structures, nomenclature, and transitions of the polymers are shown in Table I.¹ The first polymer (I) was a crystalline 10-SiB-1 which was received as a white powder. The next five structures (II-VI) were 10-SiB-3 polymers. Structures II and III were identical except for the endgroups; III was prepared from II by end-capping with $(\text{CH}_3)_3\text{SiCl}$ in ether solution. Both II and III had the appearance of candle wax. Polymer IV was a higher molecular weight 10-SiB-3 and was a cloudy viscous gum. Polymer V was similar to II with the exception that the *para*-carborane cage replaced the usual *meta*-carborane cage:



PARA



META

It was received as a brittle white wax. The last 10-SiB-3 polymer, VI, was a 1,1,1-trifluoropropyl-substituted polymer which was similar to II but with the trifluoropropyl group replacing one methyl group on each silicon atom in an atactic fashion. It was received as a viscous gum.

Polymers VII (cloudy, viscous fluid) and XI (almost clear, viscous fluid) were reported to have regular 10-SiB-4 and 10-SiB-5 structures, respectively, and XII was a commercially available, linear poly(dimethylsiloxane) (SE-30, manufactured by the General Electric Company) which was presumably end-capped and was a clear, colorless, viscous gum.

TABLE I
Nomenclature, Chemical Formulae, and Transitions of 10-SiB-x Polymers

DESIGNATION	STRUCTURE	T_m	T_{cryst}	T_g	T_{sec}	T_m/T_g
I 10-SiB-1	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \\ \\ \text{Si}-\text{CB}_{10}\text{H}_{10}-\text{C}-\text{Si}-\text{O}-\text{H} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n$	260°C	230°C	25°C	-90°C	1.78
II 10-SiB-3	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10}-\text{C}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{H} \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n$ $[\eta]_{\text{XYLENE}} = 0.15-0.20 \text{ dl/g}$ GPC PEAK MAX ~ 10-12,000	40	10	-68	-140	1.54
III 10-SiB-3 END-CAPPED	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \quad \quad \\ \text{CH}_3-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{CH}_3 \\ \quad \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$ $[\eta]_{\text{XYLENE}} = 0.15-0.20 \text{ dl/g}$ MADE FROM II	40	10	-68	-140 → -145	1.54
IV 10-SiB-3 HIGH MW	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \quad \\ \text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10}-\text{C}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{H} \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n$ $[\eta]_{\text{XYLENE}} = 0.65 \text{ dl/g}$ MW ~ 50-100,000	A	A	-70	-140	
V 10-SiB-3 PARA	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{C}_6\text{H}_5 \quad \text{C}_6\text{H}_5 \\ \quad \quad \quad \\ \text{Si}-\text{O}-\text{Si}-\text{C} \text{---} \text{C} \text{---} \text{Si}-\text{O}-\text{Si}-\text{O}-\text{H} \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{C}_{10}\text{H}_{10} \quad \text{C}_{10}\text{H}_{10} \end{array} \right]_n$ GPC PEAK MAX ~ 15,000	110	90	-35	-115	1.61
VI 10-SiB-3 FLUORINATED	$\text{HO} \left[\begin{array}{c} \text{CF}_3 \quad \text{CF}_3 \quad \text{CF}_3 \quad \text{CF}_3 \\ \quad \quad \quad \\ \text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10}-\text{C}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{H} \\ \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{C}_2\text{H}_4 \quad \text{C}_2\text{H}_4 \end{array} \right]_n$ GPC PEAK MAX ~ 8,500	A	A	-15	< -180 -90?	
VII 10-SiB-4	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \quad \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10}-\text{C}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{H} \\ \quad \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n$ GPC PEAK MAX ~ 24,000	A	A	-75	-135	
VIII 10-SiB-4 φ RANDOM	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{C}_6\text{H}_5 \\ \quad \quad \quad \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10}-\text{C}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{H} \\ \quad \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{C}_{10}\text{H}_{10} \end{array} \right]_n$ $\bar{M}_n = 12,000$ GPC PEAK MAX ~ 15-20,000 RANDOM COPOLYMER	A	A	-58	-130 → -140	
IX 10-SiB-4 φ	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{C}_6\text{H}_5 \\ \quad \quad \quad \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10}-\text{C}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{H} \\ \quad \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{C}_6\text{H}_5 \end{array} \right]_n$ GPC PEAK MAX ~ 12-18,000	A	A	-57	-140	
X 10-SiB-4 φ END-CAPPED	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{C}_6\text{H}_5 \quad \text{CH}_3 \\ \quad \quad \quad \quad \quad \\ \text{CH}_3-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{CH}_3 \\ \quad \quad \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{C}_6\text{H}_5 \quad \text{CH}_3 \end{array}$ GPC PEAK MAX ~ 12-18,000 MADE FROM IX	A	A	-57	-140	
XI 10-SiB-5	$\text{HO} \left[\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \quad \quad \quad \\ \text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{H} \\ \quad \quad \quad \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n$ GPC PEAK MAX ~ 20,000	A	A	-88	-140	
XII 10-SiB-∞ SE-30	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ $\text{MW} > 10^8$	-40	-55	-125	A	1.58

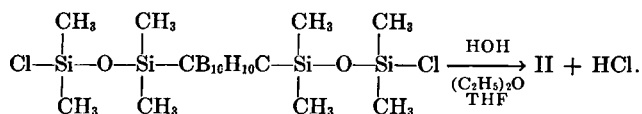
A = Absent.

Polymers VIII, IX, and X were reported to be modified 10-SiB-4 structures with 20% of the silicon atoms in the backbone having a phenyl substituent replacing one methyl group in an atactic fashion. Polymer VIII had a random placement of the phenyl-substituted silicon atoms along the chain, while IX and X were of the regular structure shown in

Table I. Polymer X was an end-capped version of IX and was prepared from IX using the procedure which was used for obtaining III. The phenyl-substituted 10-SiB-4 polymers were cloudy, viscous fluids.

Syntheses

Polymers II, V, and XI were synthesized by the simple room-temperature hydrolytic homocondensation reactions of dichloro monomers,⁶ e.g.,

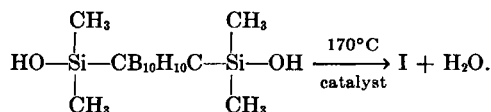


End-capping of II with $(\text{CH}_3)_3\text{SiCl}$ in $(\text{C}_2\text{H}_5)_2\text{O}$ solution yielded polymer III.⁵ When the *meta*-carborane of the monomer was replaced by the *para*-carborane cage, structure V was obtained,⁵ and when the monomer con-

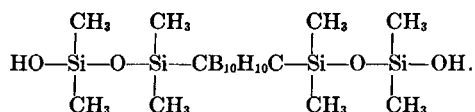
tained one additional $-\text{Si}-\text{O}-$ linkage on both sides of the *meta*-car-

$$\begin{array}{c} \text{CH}_3 \\ | \\ -\text{Si}-\text{O}- \\ | \\ \text{CH}_3 \end{array}$$

borane cage, XI was obtained. The regularity of the structures was reported to be confirmed by NMR studies.^{5,6} Polymer VIII was made by an equimolar copolymerization of $\text{Cl}_2\text{Si}(\text{C}_6\text{H}_5)(\text{CH}_3)$ with the monomer of II by the reaction shown above for the synthesis of II. The structure was considered to be random.⁶ The structure is random in the sense that although there is on average one phenylated siloxane group per repeat unit, consecutive phenylated siloxane groups are expected to occur which result in incorporation of both 10-SiB-3 units and $[-\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)-\text{O}-]_n$ ($n = 1, 2, 3, \dots$) units in the chain, as is indicated by the chemical structure of VIII shown in Table I. Polymer I was prepared by the bulk condensation of the dihydroxy monomer using tetramethylguanidine/sulfuric acid as catalyst⁵:

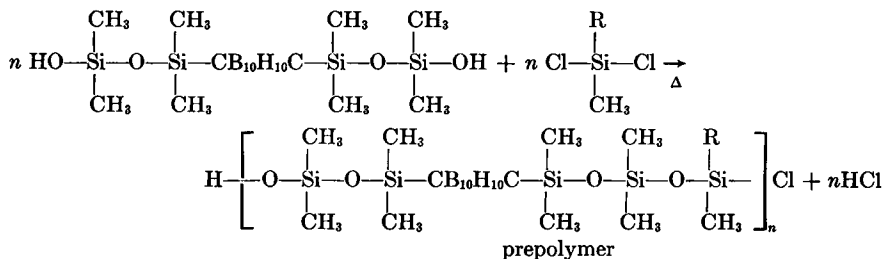


Polymer IV was prepared by the same procedure using the monomer



Polymer VI was prepared in a manner similar to IV using the dihydroxy monomer which had one $-\text{CH}_3$ group on each silicon atom replaced by $-\text{C}_2\text{H}_4\text{CF}_3$.⁷ The $-\text{C}_2\text{H}_4\text{CF}_3$ groups are expected to be placed atactically along the chain.

Polymers VII, IX, and X were synthesized (in bulk) by an initial dichloro, dihydroxy, condensation to give a prepolymer, as follows⁵:



where R = $-\text{C}_6\text{H}_5$ or $-\text{CH}_3$. The endgroup of the prepolymer (GPC peak maximum ~ 4000 , $n \sim 8$) was hydrolyzed and the resulting prepolymer was then reacted at elevated temperatures, using tetramethylguanidine/sulfuric acid as catalyst, in aromatic hydrocarbon solvents for R = $-\text{C}_6\text{H}_5$ and in bulk for R = $-\text{CH}_3$.⁵ As in the case of the other substituted polymers, the $-\text{C}_6\text{H}_5$ group is presumably placed atactically in the chain.

The poor solubility of I resulted in the polymer only being washed with hot xylene and water in its work-up. All the other polymer products were dissolved in ether, filtered, precipitated with methanol, and dried *in vacuo*.⁵

Techniques

All of the specimens for infrared analysis, except the 10-SiB-1 polymer, were cast on sodium chloride plates from 5% solutions in deuterated chloroform. The films were dried at 35°C in a vacuum oven (< 2 mm Hg). The insoluble 10-SiB-1 polymer was fabricated into a KBr pellet. The spectra were generated using a Beckman IR-12 instrument. The presence of absorption peaks at 1625 cm^{-1} and 3570 cm^{-1} in the 10-SiB-1 spectrum is presumably due to moisture in the KBr.

The proton NMR spectra of the soluble polymers (all but 10-SiB-1) were generated using a Varian HA-100 instrument. The solutions used were approximately 5% (g polymer/ml solvent) in CDCl_3 with a CHCl_3 lock signal. Chemical shifts from CHCl_3 have been translated to the " δ " scale (using a nominal shift difference between tetramethylsilane (TMS) and chloroform of 726 cycles).

RESULTS AND DISCUSSION

Infrared

There are two main absorbing segments present in the 10-SiB polymers, $[-\text{Si}(\text{R})(\text{R}')-\text{O}-]$ and the carborane unit. If these groups do not interact with each other, the resultant IR spectra would be the sum of the absorption of individual segments. If the presence of one group perturbs the other, shifts in position and intensity of peaks would be expected. Due to overlapping of critical regions, such a distinction was not made.

The model compound for $[-\text{Si}(\text{R})(\text{R}')-\text{O}-]_n$ is the polymer 10-SiB- ∞ (SE-30) the major absorption bands for which have been assigned and tabulated in Table II. The absorption band of 10-SiB- ∞ around 2960 cm^{-1} is due to C—H stretch of the Si—CH₃ group. Spectra of the small molecules, *meta*- and *para*-carborane, have also been included in Table II. These *para*- and *meta*-carboranes have a very strong band at 2600 cm^{-1} which is caused by stretch of the B—H bond. However, the characteristic absorptions of the carborane group located between 1160 and 800 cm^{-1} coincide with the broad Si—O absorption of the polysiloxane group (Table II). This complicates the assignment of peaks in the 10-SiB polymers. In most cases, absorption due to carborane units appears as shoulders or weak peaks. Typically, the 10-SiB polymers have major peaks at 2960 , 2600 , 1410 , 1260 , 1100 – 1050 , and 800 cm^{-1} which have been assigned to C—H stretch of Si—CH₃, B—H stretch of the carborane unit, —CH₂ bending, —CH₂ rocking, overlapping Si—O and carborane bands, and the Si—C band, respectively (Tables II and III).

A preliminary attempt to describe the effect of structural variables on the spectra of the 10-SiB polymers follows.

In-Chain Variations in the 10-SiB-x Structure (Figs. 1, 2, and 3)

Comparison of the spectra of 10-SiB-1, 10-SiB-3, 10-SiB-4, and 10-SiB-5 shows that the ratio of C—H to B—H absorption increases as the number of CH₃ groups per repeat unit is increased. The spectra were otherwise similar. No differences were detected among the low molecular weight, high molecular weight, end-capped, and unend-capped 10-SiB-3 samples.

Variations in the 10-SiB-3 Structure (Figs. 1 and 2)

Although there are major differences in the spectra of the small molecules, *meta*- and *para*-carborane (Table II), the spectra of the 10-SiB-3 polymers containing these carborane isomers are very similar. Comparison of the spectrum of the 10-SiB-3 *para*-polymer (V) with those of the 10-SiB-3 *meta*-polymers (II, III, IV) shows a noticeable difference in the presence of an intense peak at 955 cm^{-1} for the *para*-polymer.

The spectrum of the fluorinated 10-SiB-3 polymer (VI) contains numerous additional peaks (Table III).

Molecular weight and type of endgroup have very little effect on the IR spectra of the *meta*-10-SiB-3 polymers (cf. II, III, and IV).

Variations in the 10-SiB-4 Structure (Fig. 3)

The most pronounced differences between the spectra of the aromatic and nonaromatic 10-SiB-4 polymers are the presence of peaks at 3085 – 3000 , 1593 , 1431 , 1125 , and 750 cm^{-1} which are associated with the phenyl group (Table III).

TABLE II
 Tabulation of Prominent IR Bands of the 10-SiB-x Polymers and Related Model Compounds^a

	Stretch			CH ₂ Bending	CH ₂ Rocking	Combination of Si—O and carborane bands		Si—C of Si(CH ₃) ₂
	C—H	C—H	B—H					
10-SiB-∞ (XII)	2960 (2959) ^b	2900 (2890)		1412 (1412)	1261 (1263)	1090 (1080)	1025 (1022)	800 (800)
<i>meta</i> -Carborane ^c			2600					
<i>para</i> -Carborane ^d			2600		1160	990		
10-SiB-1 (I)	2963	2904	2600	1410	1262	1090	1020	800
10-SiB-3 (II)	2960	2900	2595	1411	1263	1090	1048	801
10-SiB-3 (III)								
end-capped	2965	2905	2600	1411	1259	1093	1047	802
10-SiB-3 (IV)								
high MW	2963	2904	2595	1410	1265	1090	1047	800
10-SiB-4 (VII)	2963	2904	2600	1411	1260	1095	1047	800
10-SiB-5 (XI)	2963	2904	2594	1410	1263	1065	1030	800
10-SiB-3 (V) <i>para</i>	2963	2904	2600	1411	1261	1050	955	803

^a Units are wave numbers (cm⁻¹); estimated limits of error are ± 2 cm⁻¹ between 700 and 2000, and ± 5 cm⁻¹ between 2000 and 4000.

^b The values inside the parentheses have been obtained from reference 8.

^c See reference 9.

^d Approximate wave numbers read from published spectrum, see reference 10.

^e Complicated peaks and shoulders.

TABLE III
Tabulation of Phenylated 10-SiB-4 and Fluorinated 10-SiB-3 Polymers

	Aromatic H	Stretch			Aromatic C—C	CH ₂ Bend- ing	CH ₂ Rock- ing	Aroma- tic	Combination of Si—O and carborane bands	Si—C	Extra bands for VI
		C—H	C—H	B—H							
10-SiB-4 ϕ random (VIII)	3075	2963	2905	2594	1593	1410	1263	1125	1103	1045	801
10-SiB-4 ϕ (IX)	3087	2965	2904	2600	1593	1410	1263	1125	1103	1046	801
10-SiB-4 ϕ end-capped (X)	3075	2963	2904	2594	1593	1410	1263	1125	1104	1046	801
10-SiB-3 fluorinated (VI)		2962	2904	2600			1267		1100	1050	1446, 1422, 1371, 1316, 1211, 1133, 1030, 897, 839, 810, 769,

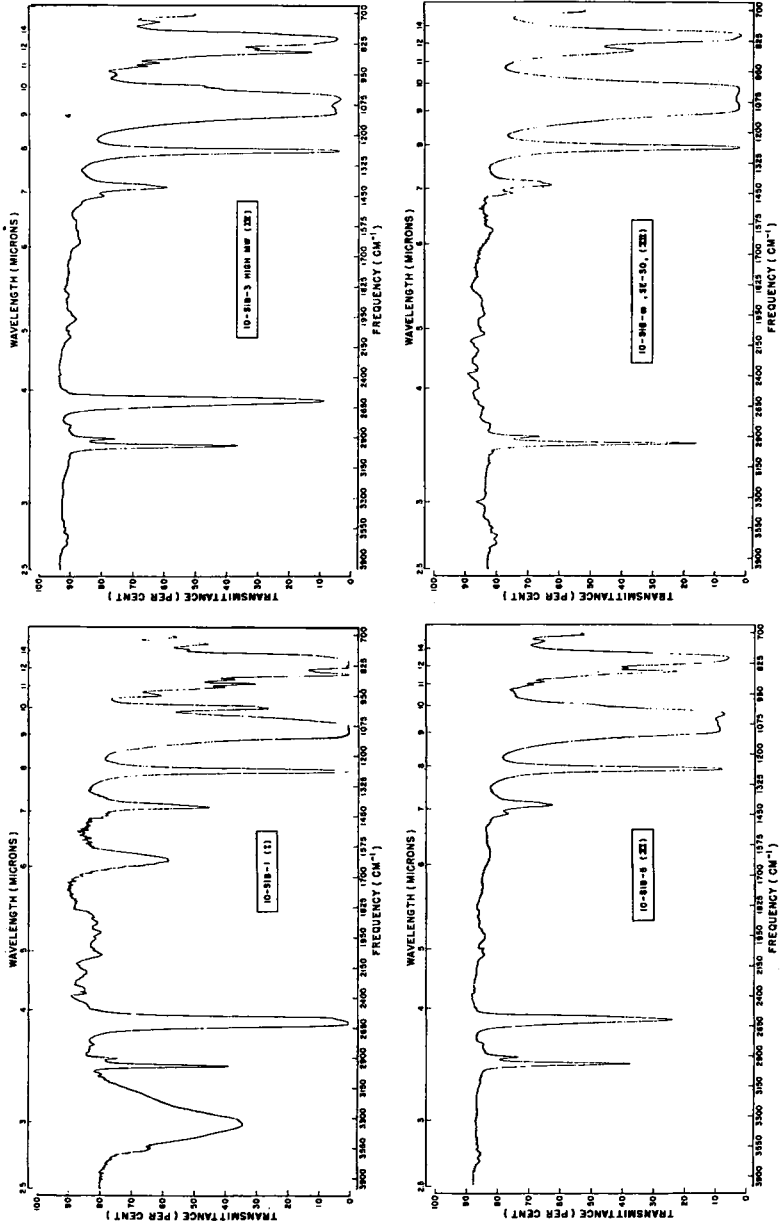


Fig. 1. 10-SiB-x Polymers: · infrared spectra (see Fig. 3 for 10-SiB-4).

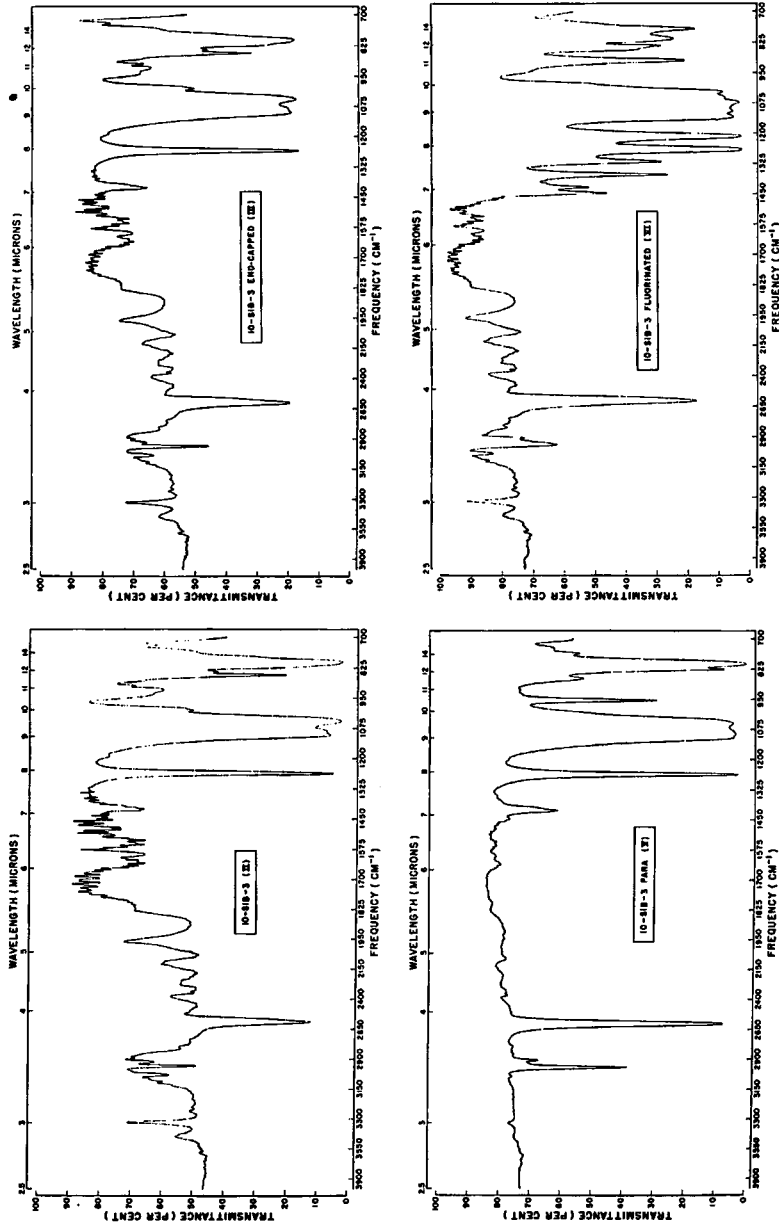


Fig. 2. 10-SIB-3 Polymers: infrared spectra.

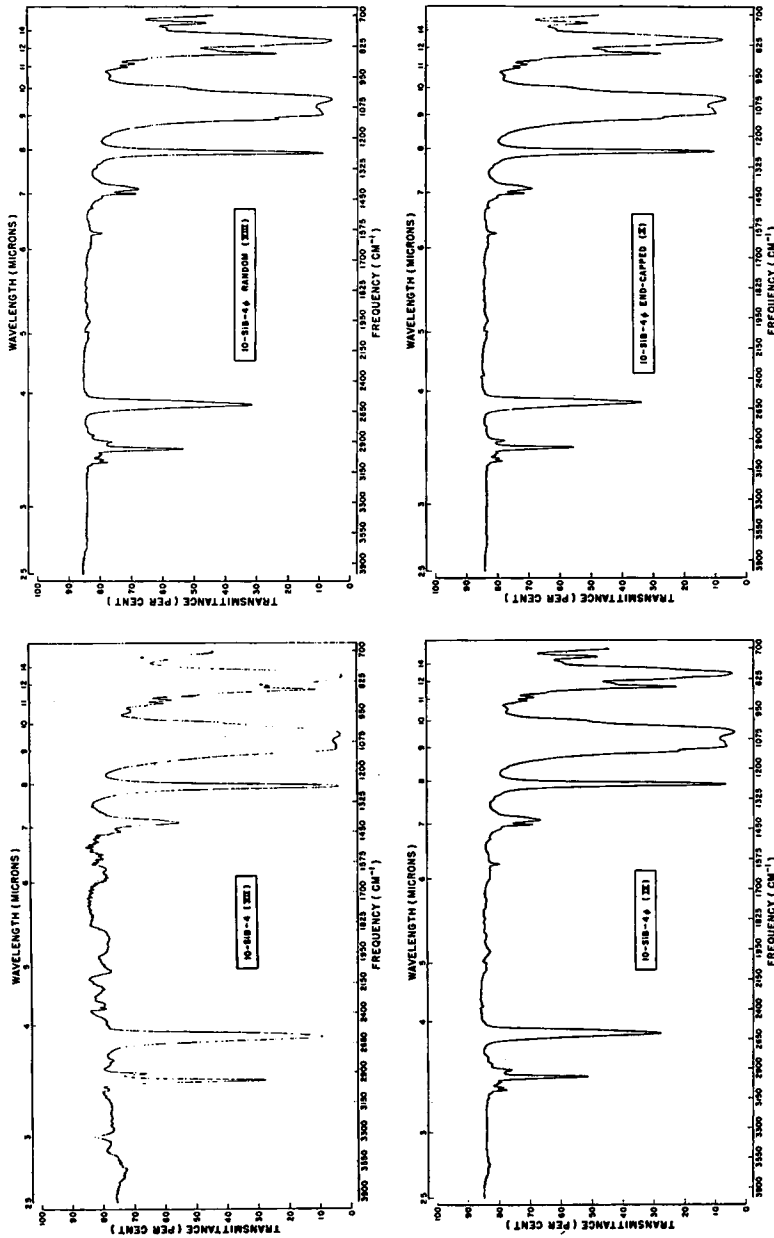
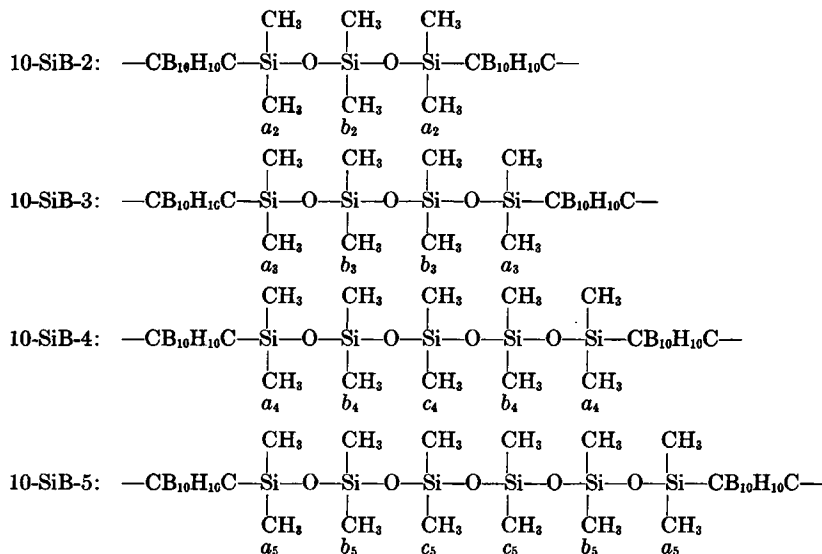


Fig. 3. 10-SiB-4 Polymers: infrared spectra.

Nuclear Magnetic Resonance

The different types of methyl groups in the *meta*-10-SiB-x polymers are shown as follows:



where $\text{---CB}_{10}\text{H}_{10}\text{C---}$ represents the *meta*-carborane cage. A general pattern emerges from consideration of the NMR spectra of the polymers which shows that the *meta*-carborane cage interacts with the silyl-methyl groups causing a downfield shift. This deshielding effect of the *meta*-carborane cage is much greater than that of the oxygen atom and decreases with distance from the *meta*-carborane cage. Thus, in the *meta*-10-SiB-x polymer series, the chemical shifts are in the order a 's $>$ b 's $>$ c 's, which is consistent with studies of model compounds.¹¹ It is to be expected that the individual members of each of the a , b , and c groups of methyl protons have different chemical shifts in consequence of differences in symmetry and differences in distance from the electronegative centers. For example, although a_2 , a_3 , a_4 , and a_5 have one *meta*-carborane cage in their immediate proximity, the second *meta*-carborane cages are 2, 3, 4, and 5 siloxane groups away from the respective silylmethyl groups. Thus, the chemical shift within the group should have the following order:

$$Z_x > Z_{x+1} > Z_{x+2}, \text{ etc.}$$

where Z = the chemical shift the a , b , or c silylmethyl protons in the 10-SiB-x polymers. In this connection it is noteworthy that the *para*-carborane cage (in *para*-10-SiB-3) exerts a shielding effect on the methyl protons.

In-Chain Variations in the 10-SiB-x Structure (Figs. 4 and 5)

The methyl proton NMR spectrum of the 10-SiB-1 polymer was not obtained because of lack of solubility.

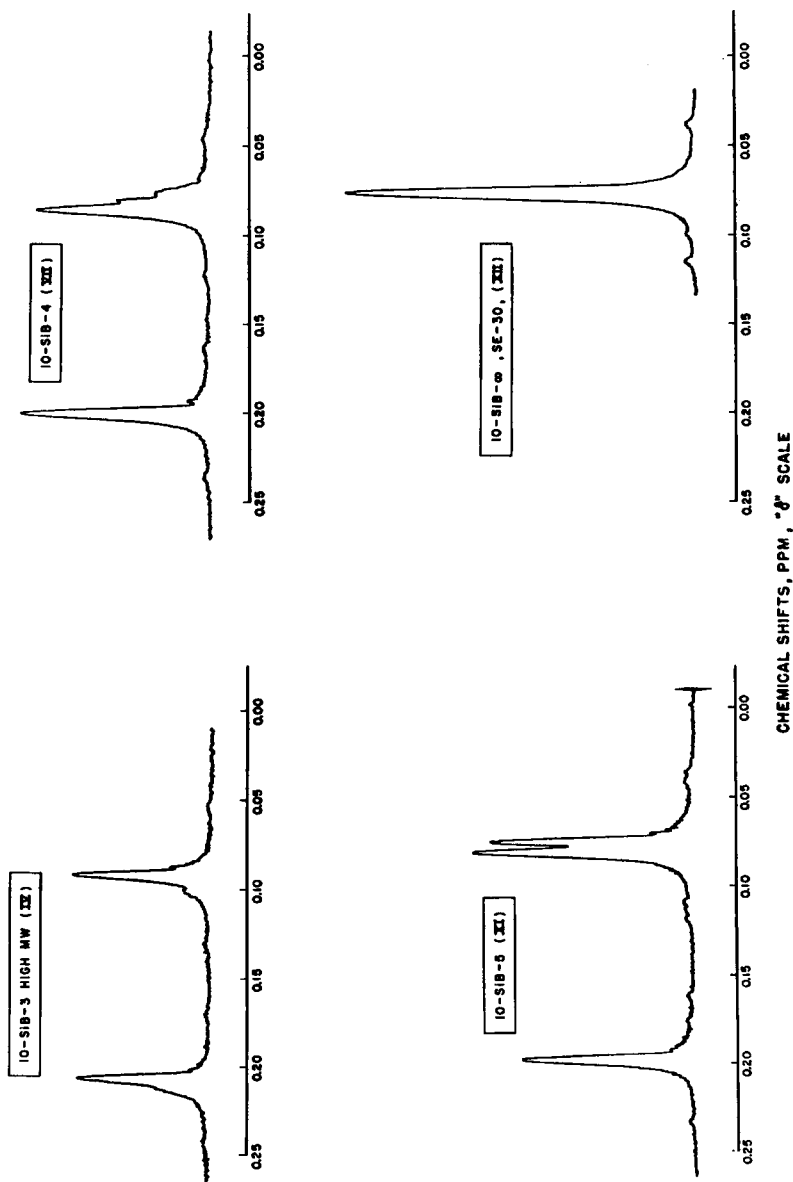


Fig. 4. 10-SiB-x Polymers: methyl proton NMR spectra (100 MHz).

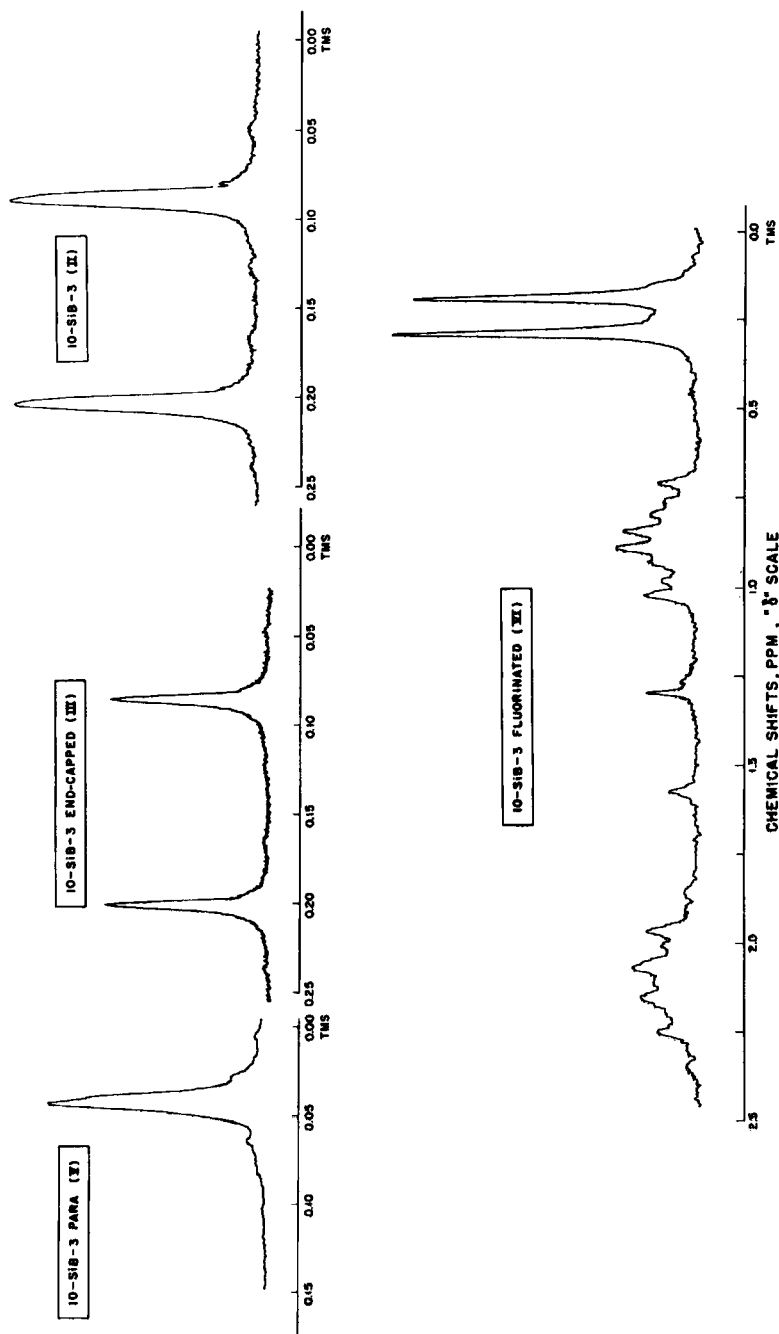


Fig. 5. 10-SIB-3 Polymers: methyl proton NMR spectra (100 MHz).

The spectrum (not shown) of a sample of 10-SiB-2 shows two peaks¹²; that at lower field is twice as intense as the other. Consideration of the structure shows that the ratio of a_2 to b_2 methyl protons is 2 to 1. Therefore, the stronger (downfield) signal is due to the a_2 type methyl protons.

The methyl proton NMR spectra of the *meta*-10-SiB-3 polymers (II, III, and IV) contain two peaks of equal intensity at 0.20 ± 0.005 and 0.09 ± 0.005 ppm relative to TMS, which are assigned to the a_3 and b_3 methyl groups, respectively. Comparison of spectra of polymers II, III, and IV shows that neither end-capping nor increasing the molecular weight significantly affects the NMR spectra of the *meta*-10-SiB-3 polymers.

Polymer 10-SiB-5 has three peaks in its NMR spectrum. The two upfield peaks, at 0.07 ± 0.005 and 0.08 ± 0.005 ppm, are assigned to the c_5 and b_5 methyls, respectively. The sum of their intensities is twice that of the a_5 methyl peak, 0.20 ± 0.005 ppm.

Consideration of the structure of the 10-SiB-4 polymer (VII) shows that there are three dissimilar methyl groups: a_4 , b_4 , and c_4 . The intensity ratio of the a_4 signal to that of remaining $b_4 + c_4$ signals is expected to be 1:1.5. The NMR spectrum of the 10-SiB-4 polymer has two major peaks at $\delta = 0.20 \pm 0.005$ ppm and 0.09 ± 0.005 ppm. There are also two smaller bands at $\delta = 0.08 \pm 0.005$ ppm and 0.07 ± 0.005 ppm which appear as shoulders upfield from the center of the latter peak. The intensity ratio of the peak at $\delta = 0.20 \pm 0.005$ ppm, due to a protons, to that of the remaining protons is 1:1.3. The low ratio of $[(b+c)/a]$ methyl signals indicates that the amount of c_4 [$-\text{Si}(\text{CH}_3)_2-\text{O}-$] which is incorporated into the polymer is lower than is to be expected on a stoichiometric basis. The presence of an extra band indicates that a pure 10-SiB-4 structure may not be present. An explanation for this discrepancy should arise from examination of the synthetic route.

The results of the gel permeation chromatogram on the prepolymer show that about eight repeat units are coupled in a 10-SiB-4 fashion.⁵ Prepolymer units are then coupled in a fashion that would yield 10-SiB-4, 10-SiB-3, and 10-SiB-5 bridges (in the approximate ratio 2:1:1) between the prepolymer units (see "Syntheses"). Therefore, signals due to units other than of 10-SiB-4 are to be expected. This structural complication should not affect the $a:b:c$ ratio of methyl groups. It is therefore apparent that there are competitive reactions which prevent stoichiometric incorporation of the dimethylsilyl group into the prepolymer and consequently into the polymer.

The chemical shift for c_4 of 10-SiB-4 (assigned to 0.07 ppm) is indistinguishable from the single resonance of 10-SiB- ∞ .

Variations in the 10-SiB-3 Structure (Figs. 4 and 5)

The totally methylated 10-SiB-3 *meta*-carborane polymers (II, III, and IV) have been discussed.

Examination of the proposed structure for *para*-10-SiB-3 shows that there are two kinds of methyl groups, a_3 and b_3 , in this polymer. The

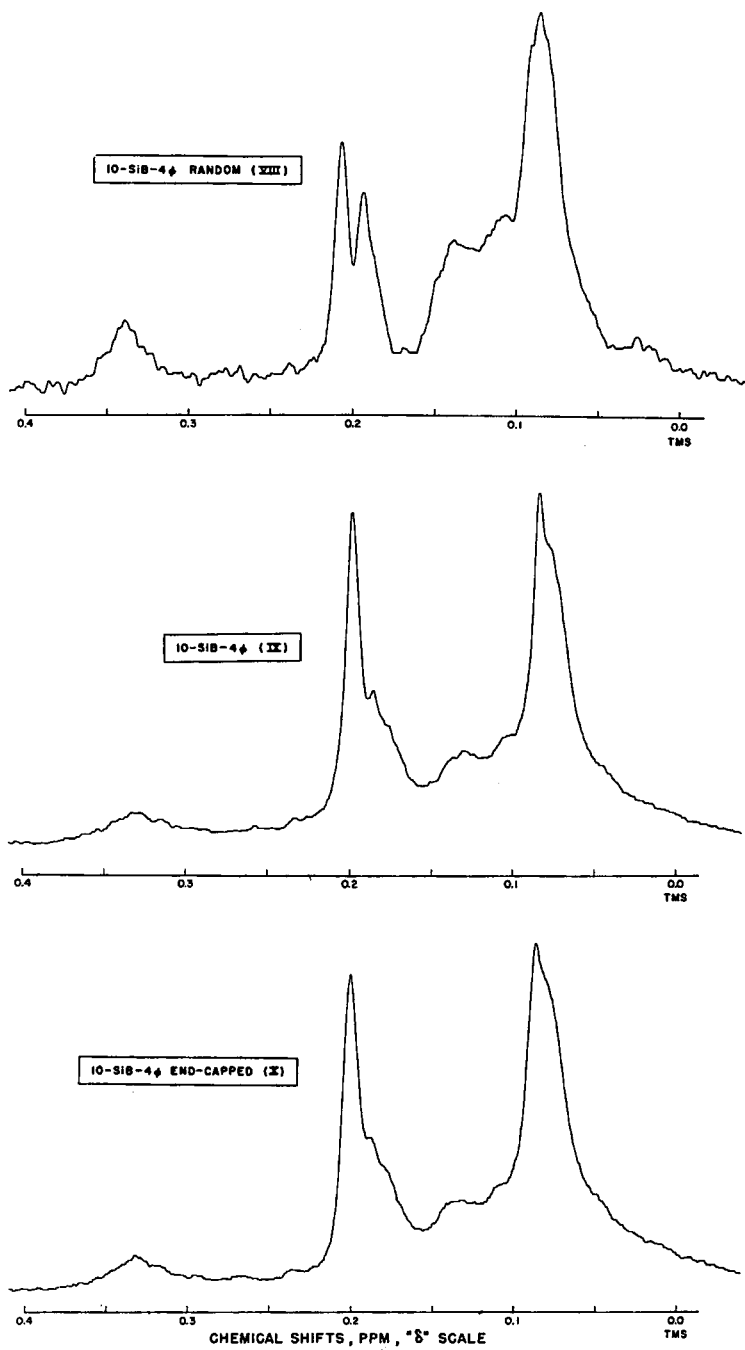


Fig. 6. 10-SiB-4 Polymers: methyl proton NMR spectra (100 MHz).

methyl proton NMR spectrum has only one resolved peak around 0.04 ± 0.005 ppm. This indicates not only that a_3 and b_3 methyl groups experience similar environments (the one peak detected is not a singlet, it is skewed), but that they are also much less deshielded than the b_3 methyl groups in the *meta*-10-SiB-3 polymer and even the methyl group in poly(dimethylsiloxane).

The proton NMR spectrum of the fluorinated 10-SiB-3 polymer has a rather complex structure. The electronegative- CF_3 group deshields the dimethylene and the methyl groups. The resonances of the methyl protons on the silicon atoms which contain the fluorinated group, for example, occur at 0.19 ± 0.005 and 0.29 ± 0.005 ppm which are much further downfield than those of the methylated 10-SiB-3 polymers. Strong splitting between the nonequivalent protons of the trifluoropropyl groups results in a very complex spectrum downfield from the two methyl peaks.

Variations in the 10-SiB-4 Structure (Fig. 6)

Polymer 10-SiB-4 itself has been discussed.

To obtain random and regular structures for the phenylated polymers, two different synthetic routes have been employed. For the regular 10-SiB-4 ϕ structure, the synthetic route used for 10-SiB-4 was employed, substituting dichloromethylphenylsilane for dichlorodimethylsilane. The random 10-SiB-4 ϕ was synthesized by an equimolar copolymerization of dichloro-10-SiB-3 monomer with dichloromethylphenylsilane in the presence of water.⁶ These polymers (VIII, IX, X) were reported to contain on average one $-\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)-\text{O}-$ group per repeat unit.^{5,6} The phenyl group shifts the signal of the methyl group which is on the same silicon atom downfield: the signal at 0.34 ± 0.005 ppm for the random polymer and 0.33 ± 0.005 ppm for regular polymers (IX and X) have been assigned to this methyl group. This assignment agrees quite well with that of a model monomeric compound.¹¹

Comparison of the intensity of the signals at 0.33 ppm to signals of the remaining methyl groups for the "regular" polymers (IX and X), however, indicates that a lower than expected portion of phenylmethylsiloxane has been incorporated into the polymer during synthesis (as for the 10-SiB-4 polymer). Examination of a 60 MHz spectrum (not shown) indicates that the ratio of $-\text{C}_6\text{H}_5$ to $-\text{CH}_3$ in the "random" polymer fits the proposed stoichiometry as previously reported.⁶ On the other hand, for the "regular" polymers this ratio is about 0.8 of the value which is to be expected.

SUMMARY

Spectral analysis shows that the various 10-SiB-3 and the 10-SiB-5 polymers have the anticipated structures. No ambiguity in structure was to be expected for these and for the 10-SiB-1 polymer, since the syntheses involved one-step homocondensations of symmetrical difunctional monomers.

The random 10-SiB-4 ϕ polymer, synthesized by an equimolar one-step co-condensation, had the anticipated structure. On the other hand, the "regular" 10-SiB-4 polymers, which were made by using two consecutive steps, were structurally and stoichiometrically deficient.

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