#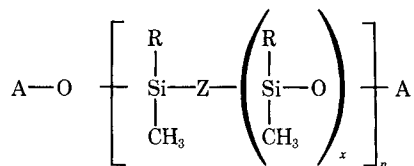 High-Temperature Elastomers: A Systematic Series of Linear Poly(Carborane-Siloxane)s Containing Icosahedral (—CB$_{10}$H$_{10}$C—) Cages. I. Thermomechanical Behavior in Nitrogen

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Synopsis

An extensive study of structure–bulk property relations for a systematic series of well-defined linear poly(carborane-siloxane)s is reported. These polymers form the backbone components of the most recently developed high-temperature elastomers. The basic structure is

$$A\text{—}O \left[\begin{array}{c} R \\ | \\ Si\text{—}Z\text{—} \\ | \\ CH_3 \end{array} \left(\begin{array}{c} R \\ | \\ Si\text{—}O \\ | \\ CH_3 \end{array} \right)_x \right]_n A$$

where (1) $x = 1, 3, 4, 5, \infty$; (2) A = endgroups (reactive and inert); (3) Z = *meta*-, *para*-carborane (for $x = 3$); (4) R = —CH$_3$, R = —C$_2$H$_4$CF$_3$ (for $x = 3$), one in five R = —C$_6$H$_5$ with the remainder —CH$_3$ (for $x = 4$, randomly and regularly substituted); (5) molecular weight = ∼10,000, ∼50,000 (for $x = 3$). Thermomechanical spectra (∼1 cps) from −180°C to 625°C to −180°C in nitrogen at 3.6°C/min and thermogravimetric data from 25°C to 800°C in argon are presented. Physical transitions (T_g, T_m, T_{crys}, T_{sec}) are discussed, including a correlation of T_g data with structure (for $x = 1, 2, 3, 4, 5, \infty$) using a copolymer equation. Thermostability is also discussed in terms of structure.

INTRODUCTION

The search for high-temperature elastomers has led to the development and marketing of the carborane-siloxane polymers.   Most of the work to date has involved incorporation of the 10-boron *meta*-carborane cage into a dimethylsiloxane backbone.   Current and potential applications of these materials are claimed to be far reaching.   A high-purity grade of one of them is available from Analabs Inc., North Haven, Connecticut, under the name Dexsil 300-GC (10-SiB-3, see below) for use as a liquid substrate for vapor-phase chromatographic columns.   This system has been used for separating high-boiling materials such as silicone oils, poly-

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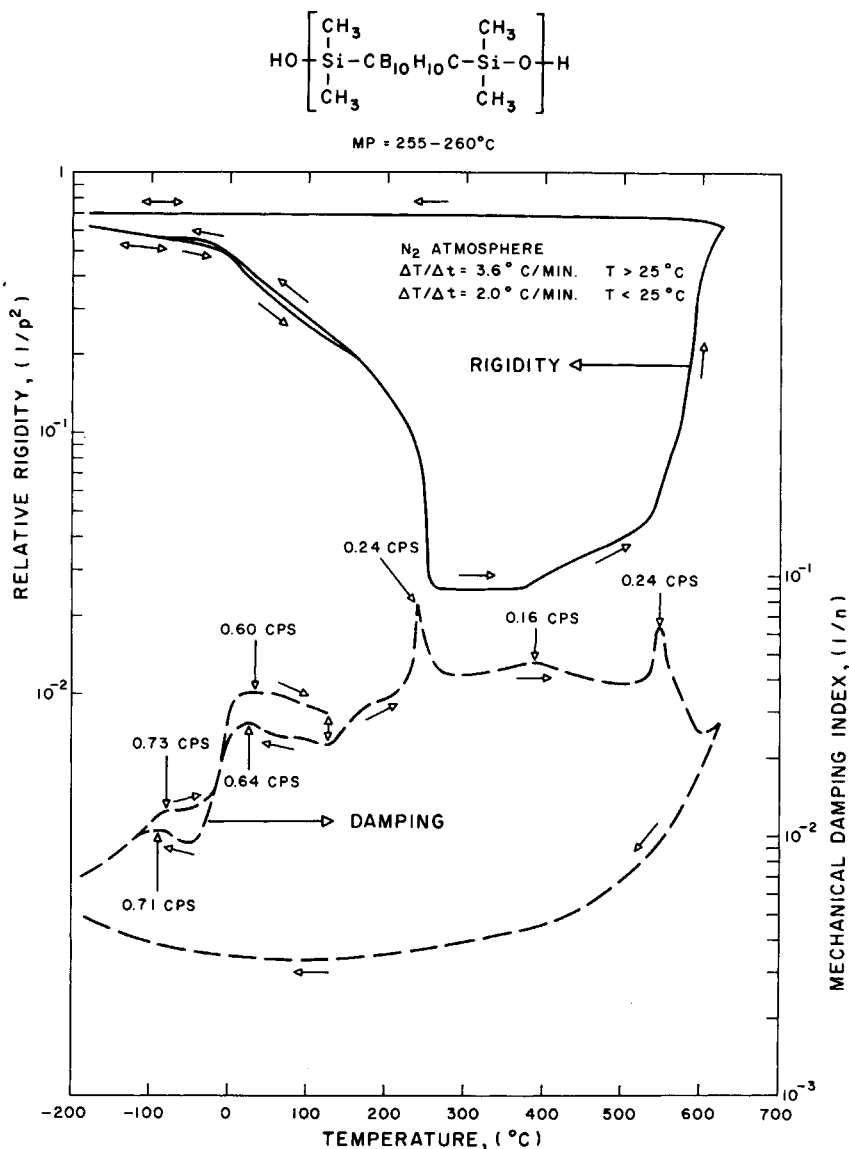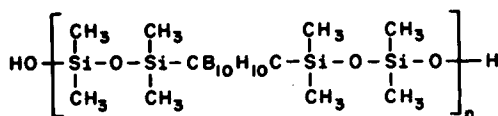* Present address: Bell Laboratories, Whippany, New Jersey 07981.

Fig. 1. 10-SiB-1: thermomechanical spectra in nitrogen ($\Delta T/\Delta t = 3.6°C/min$, $T > 25°C$; $\Delta T/\Delta t = 2°C/min$, $T < 25°C$) from $130°$ to $-180°$ to $625°$ to $-180°$ to $25°C$.

phenyl ethers, butter triglycerides, and pesticides at temperatures up to 500°C. Another material (a modified, low molecular weight 10-SiB-2) is being used to coat metals, glass, and fabrics. Application via xylene solution and air cure at elevated temperature results in a thin, tough film. Potential applications include protection of autoclave interiors, furnace parts, and electrical components.[1] Trifluoropropyl-substituted materials are being explored as high-temperature sealants for fuel tanks.[2]
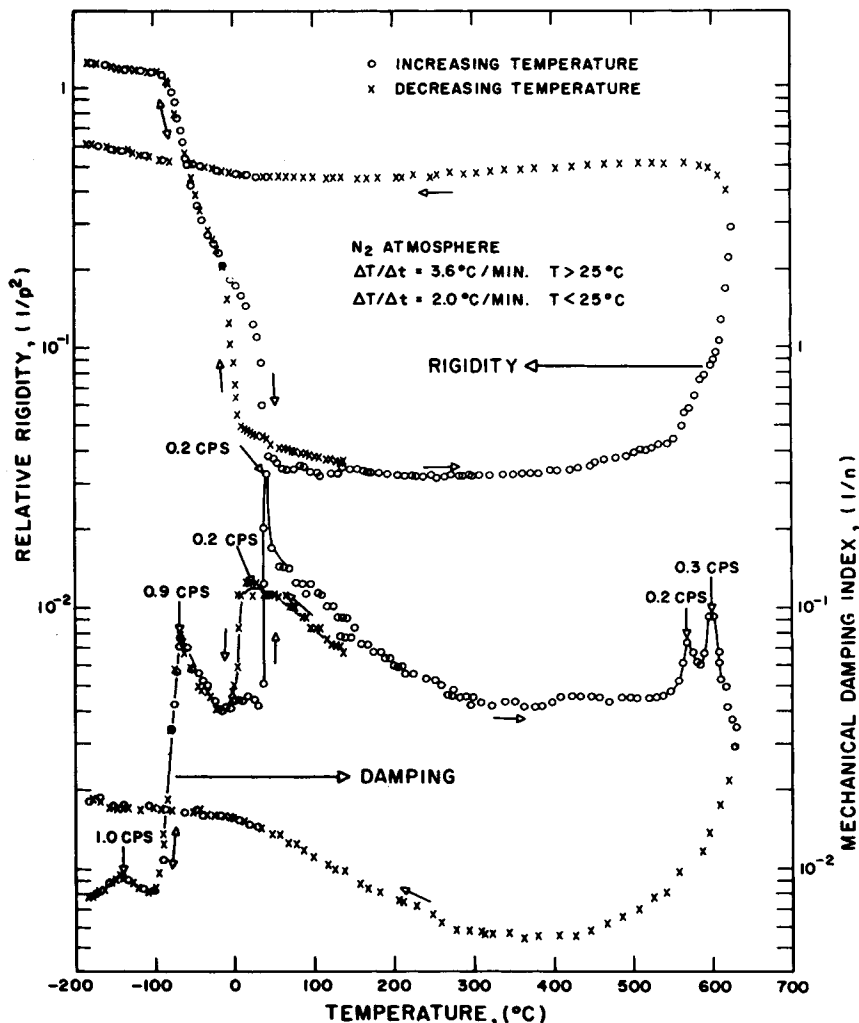
Fig. 2. 10-SiB-3: thermomechanical spectra in nitrogen ($\Delta T/\Delta t$ = 3.6°C/min, T > 25°C; $\Delta T/\Delta t$ = 2°C/min, T < 25°C) from 130° to −180° to 625° to −180° to 25°C.

The 12 linear polymers which are discussed herein represent one of the most comprehensive series of systematically varying structures in the field of elastomers. Differences include in-chain variations of the polymeric repeat unit as well as variations in side groups, endgroups, molecular weight, and regularity of the repeat unit. The influences of the varia-
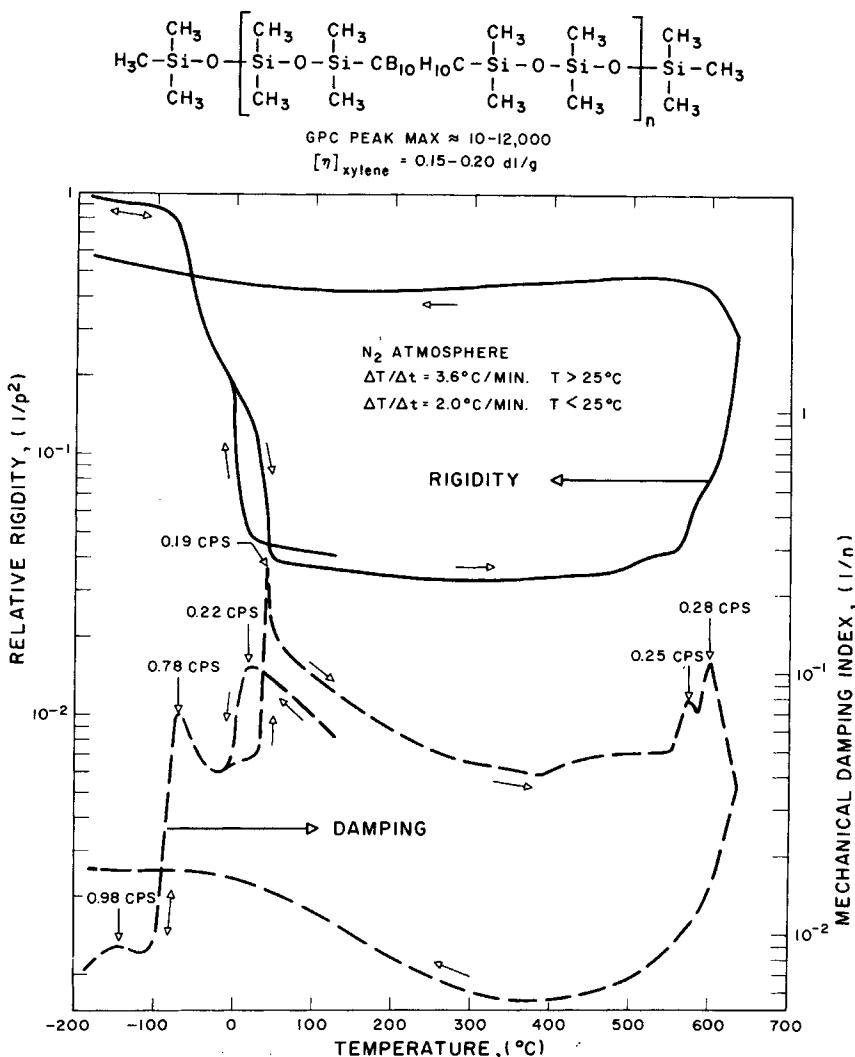
$$H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\left[\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CB_{10}H_{10}C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O\right]_n\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CH_3$$

GPC PEAK MAX $\approx$ 10–12,000

$[\eta]_{xylene}$ = 0.15–0.20 dl/g

Fig. 3. 10-SiB-3 End-Capped: thermomechanical spectra in nitrogen ($\Delta T/\Delta t$ = 3.6°C/min, T > 25°C; $\Delta T/\Delta t$ = 2°C/min, T < 25°C) from 130° to −180° to 625° to −180° to 25°C.

tions in molecular structure were studied thermomechanically with respect to their bearing upon both physical transitions and high-temperature thermal stability in an inert atmosphere.

EXPERIMENTAL

Materials

The polymers whose mechanical spectra are reported and discussed in this report were synthesized, molecularly characterized, and supplied by
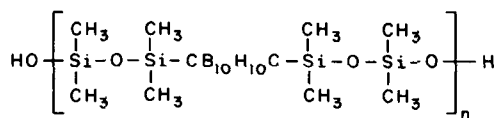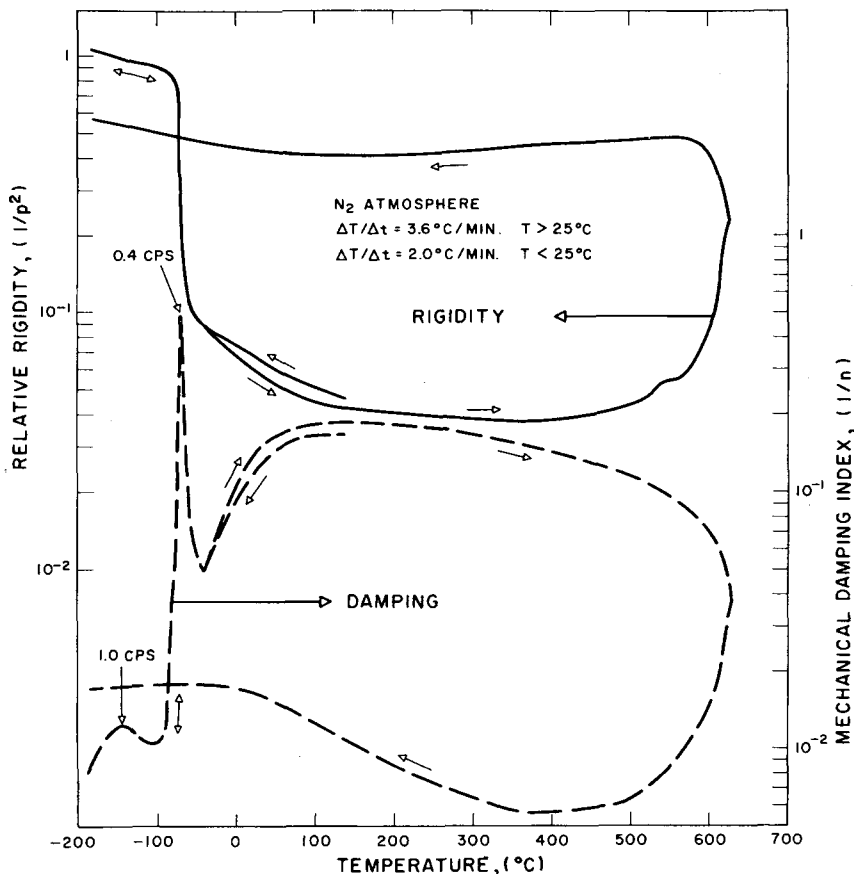
Fig. 4. 10-SiB-3 High Molecular Weight: thermomechanical spectra in nitrogen $(\Delta T/\Delta t = 3.6°C/min, T > 25°C; \Delta T/\Delta t = 2°C/min, T < 25°C)$ from $130°$ to $-180°$ to $625°$ to $-180°$ to $25°C$.

the Olin Corporation Research Center, New Haven, Connecticut.[1-6] The structures, nomenclature, and transitions of these polymers are shown in Table I. The thermomechanical spectra which were used to determine the transitions are shown in Figures 1–12. 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. Structure III was prepared from II by end-capping with $(CH_3)_3SiCl$ in ether solution. Both II and III had the appearance of candle wax. Polymer IV was a higher molecu-

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

	DESIGNATION	STRUCTURE	T_m	T_{crys}	T_g	T_{sec}	T_m/T_g
I	10-SiB-1	$HO+Si(CH_3)_2-CB_{10}H_{10}C-Si(CH_3)_2-O+_nH$	260°C	230°C	25°C	-90°C	1.78
II	10-SiB-3	$HO+Si(CH_3)_2-O-Si(CH_3)_2-CB_{10}H_{10}C-Si(CH_3)_2-O-Si(CH_3)_2-O+_nH$ $[\eta]_{XYLENE} = 0.15-0.20 \ dl/g$ GPC PEAK MAX. ~ 10-12,000	40	10	-68	-140	1.54
III	10-SiB-3 END-CAPPED	$CH_3-Si(CH_3)_2-O+Si(CH_3)_2-O-Si(CH_3)_2-CB_{10}H_{10}C-Si(CH_3)_2-O-Si(CH_3)_2-O+_n Si(CH_3)_2-CH_3$ $[\eta]_{XYLENE} = 0.15-0.20 \ dl/g$ MADE FROM II	40	10	-68	-140 → -145	1.54
IV	10-SiB-3 HIGH MW	$HO+Si(CH_3)_2-O-Si(CH_3)_2-CB_{10}H_{10}C-Si(CH_3)_2-O-Si(CH_3)_2-O+_nH$ $[\eta]_{XYLENE} = 0.65 \ dl/g$ MW ~ 50-100,000	A	A	-70	-140	
V	10-SiB-3 PARA	$HO+Si(CH_3)_2-O-Si(CH_3)_2-C_6H_{10}-C-Si(CH_3)_2-O-Si(CH_3)_2-O+_nH$ GPC PEAK MAX. ~ 15,000	110	90	-35	-115	1.61
VI	10-SiB-3 FLUORINATED	$HO+Si(C_2H_4CF_3)_2-O-Si(C_2H_4CF_3)_2-CB_{10}H_{10}C-Si(CH_3)_2-O-Si(CH_3)_2-O+_nH$ GPC PEAK MAX. ~ 8,500	A	A	-15	<-180 -90?	
VII	10-SiB-4	$HO+Si(CH_3)_2-O-Si(CH_3)_2-CB_{10}H_{10}C-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2-O+_nH$ GPC PEAK MAX. ~ 24,000	A	A	-75	-135	
VIII	10-SiB-4 φ RANDOM	$HO+[Si(CH_3)_2-O-Si(CH_3)_2-CB_{10}H_{10}C-Si(CH_3)_2-O-Si(CH_3)_2-O]_{0.5}[Si(C_6H_5)(CH_3)-O]_{0.5}+_nH$ $\bar{M}_n = 12,000$ GPC PEAK MAX. ~ 15-20,000 RANDOM COPOLYMER	A	A	-58	-130 → -140	
IX	10-SiB-4 φ	$HO+Si(CH_3)_2-O-Si(CH_3)_2-CB_{10}H_{10}C-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(C_6H_5)(CH_3)-O+_nH$ GPC PEAK MAX. ~ 12-18,000	A	A	-57	-140	
X	10-SiB-4 φ END-CAPPED	$CH_3-Si(CH_3)_2-O+Si(CH_3)_2-O-Si(CH_3)_2-CB_{10}H_{10}C-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(C_6H_5)(CH_3)-O+_n Si(CH_3)_2-CH_3$ GPC PEAK MAX. ~ 12-18,000 MADE FROM IX	A	A	-57	-140	
XI	10-SiB-5	$HO+Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2-CB_{10}H_{10}C-Si(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2-O+_nH$ GPC PEAK MAX. ~ 20,000	A	A	-88	-140	
XII	10-SiB-∞ SE-30	$CH_3-Si(CH_3)_2-O+Si(CH_3)_2-O+_n Si(CH_3)_2-CH_3$ MW > 10^6	-40	-55	-125	A	1.58

A = ABSENT

lar weight 10-SiB-3 which had been prepared by a different synthesis (see below) and was a cloudy viscous gum. Polymer V was similar to II, with the exception that the *para*-carborane cage (B) replaced the usual *meta*-carborane cage (A). It was received as a brittle white wax.

$$-CB_{10}H_{10}C-$$
META

A

$$-C \underset{B_{10} \ H_{10}}{\overset{\bigcirc}{C}}-$$
PARA

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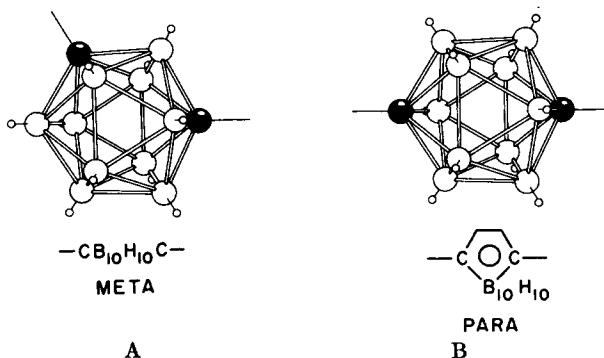
The last 10-SiB-3 polymer, VI, was a 1,1,1-trifluoropropyl-substituted polymer which was similar to II but with the trifluoropropyl group replacing one methyl group on each silicon atom in an atactic fashion. It was received as a viscous gum.

Polymers VII (cloudy, viscous fluid) and XI (almost clear, viscous fluid) had regular 10-SiB-4 and 10-SiB-5 structures, 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 water-white, viscous gum.

Polymers VIII, IX, and X were 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 (see below). 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,[3] e.g.,

$$\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Cl-Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-CB_{10}H_{10}C-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-Cl \xrightarrow[\underset{THF}{(C_2H_5)_2O}]{HOH} II + HCl$$
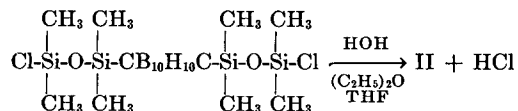
End-capping of II with $(CH_3)_3SiCl$ in $(C_2H_5)_2O$ solution yielded III.[4] When the *meta*-carborane cage of the monomer was replaced by the *para*-carborane cage, structure V was obtained,[4] and when the monomer con-

$$HO \left[\begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{array} \begin{array}{c} CH_3 \\ | \\ Si-C \\ | \\ CH_3 \end{array} \middle\langle \bigcirc \middle\rangle \begin{array}{c} \\ C \\ B_{10}H_{10} \end{array} \begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{array} \begin{array}{c} CH_3 \\ | \\ Si-O \\ | \\ CH_3 \end{array} \right]_n H$$

GPC PEAK MAX. ≈ 15,000
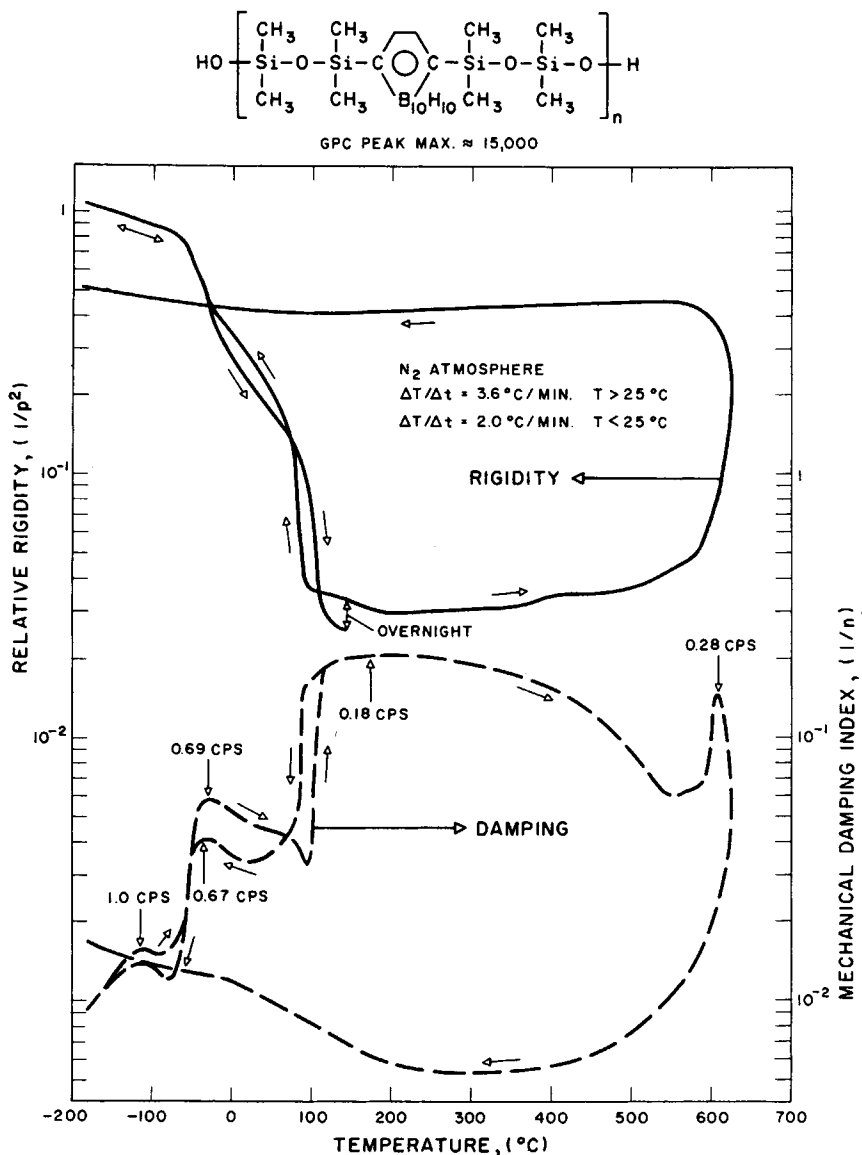
Fig. 5. 10-SiB-3 Para: thermomechanical spectra in nitrogen ($\Delta T/\Delta t$ = 3.6°C/min, $T > 25$°C; $\Delta T/\Delta t$ = 2°C/min, $T < 25$°C) from 130° to −180° to 625° to −180° to 25°C.

tained one additional —Si—O— linkage on each side of the —$CB_{10}H_{10}C$—cage, XI was obtained. The regularity of the structures was confirmed by NMR studies.[3] Polymer VIII was made by an equimolar copolymerization of $Cl_2Si(C_6H_5)(CH_3)$ with the monomer of II by the reaction shown above for the synthesis of II. The structure was considered to be random[3] in the sense that although there is on average one phenylated siloxane group
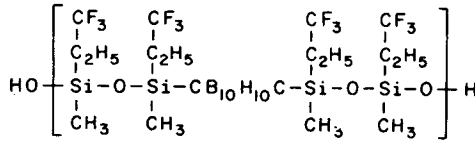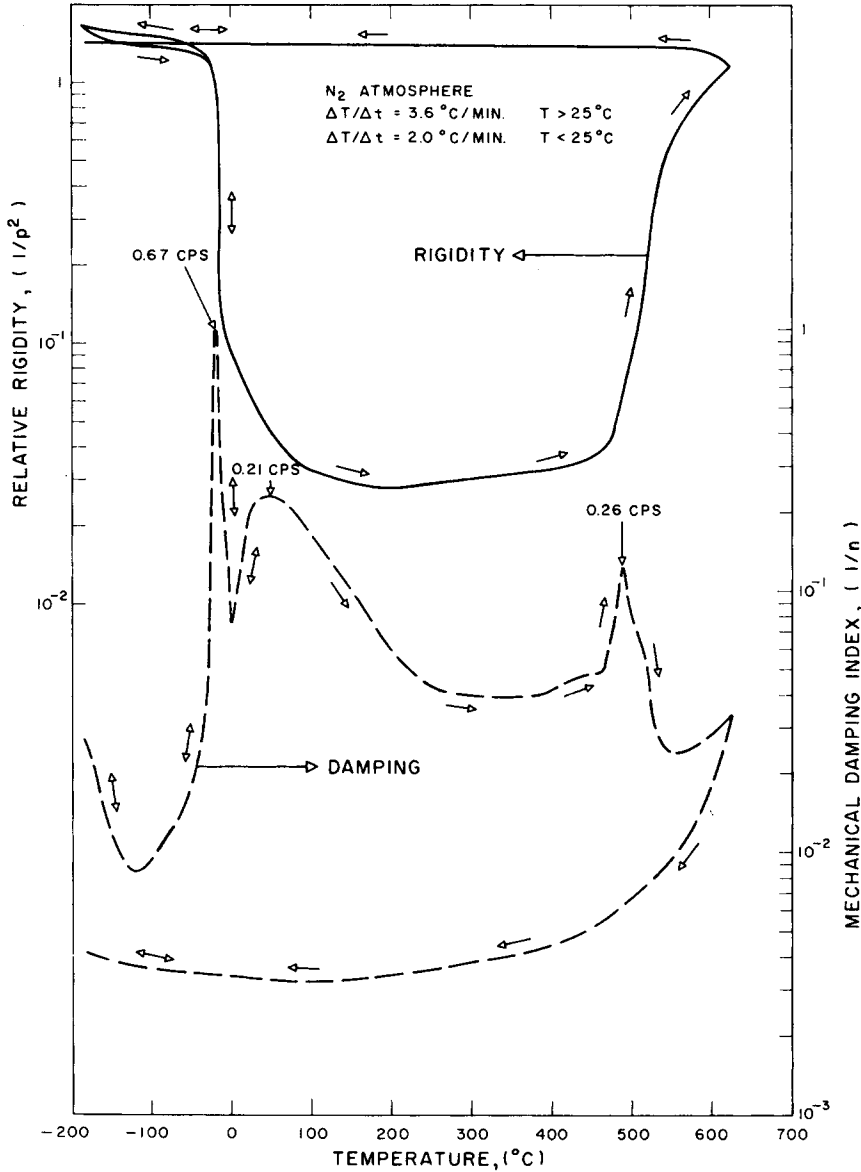
Fig. 6. 10-SiB-3 Fluorinated: thermomechanical spectra in nitrogen ($\Delta T/\Delta t$ = 3.6°C/min, $T > 25$°C; $\Delta T/\Delta t$ = 2°C/min, $T < 25$°C) from 130° to −180° to 625° to −180° to 25°C.

per repeat unit, consecutive phenylated siloxane groups are expected to occur which result in incorporation of both 10-SiB-3 units and [—Si(CH₃)-(C₆H₅)—O—]ₙ $(n = 1,2,3,...)$ units in the chain, as is indicated by the chemical structure of VIII shown in Table I. Polymer I was prepared by

$$\text{HO}\left[\begin{array}{cccccc} \text{CH}_3 & \text{CH}_3 & & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\ | & | & & | & | & | \\ \text{Si-O-Si-CB}_{10}\text{H}_{10}\text{C-Si-O-Si-O-Si-O} \\ | & | & & | & | & | \\ \text{CH}_3 & \text{CH}_3 & & \text{CH}_3 & \text{CH}_3 & \text{CH}_3 \end{array}\right]_n \text{H}$$

GPC PEAK MAX. ≈ 24,000
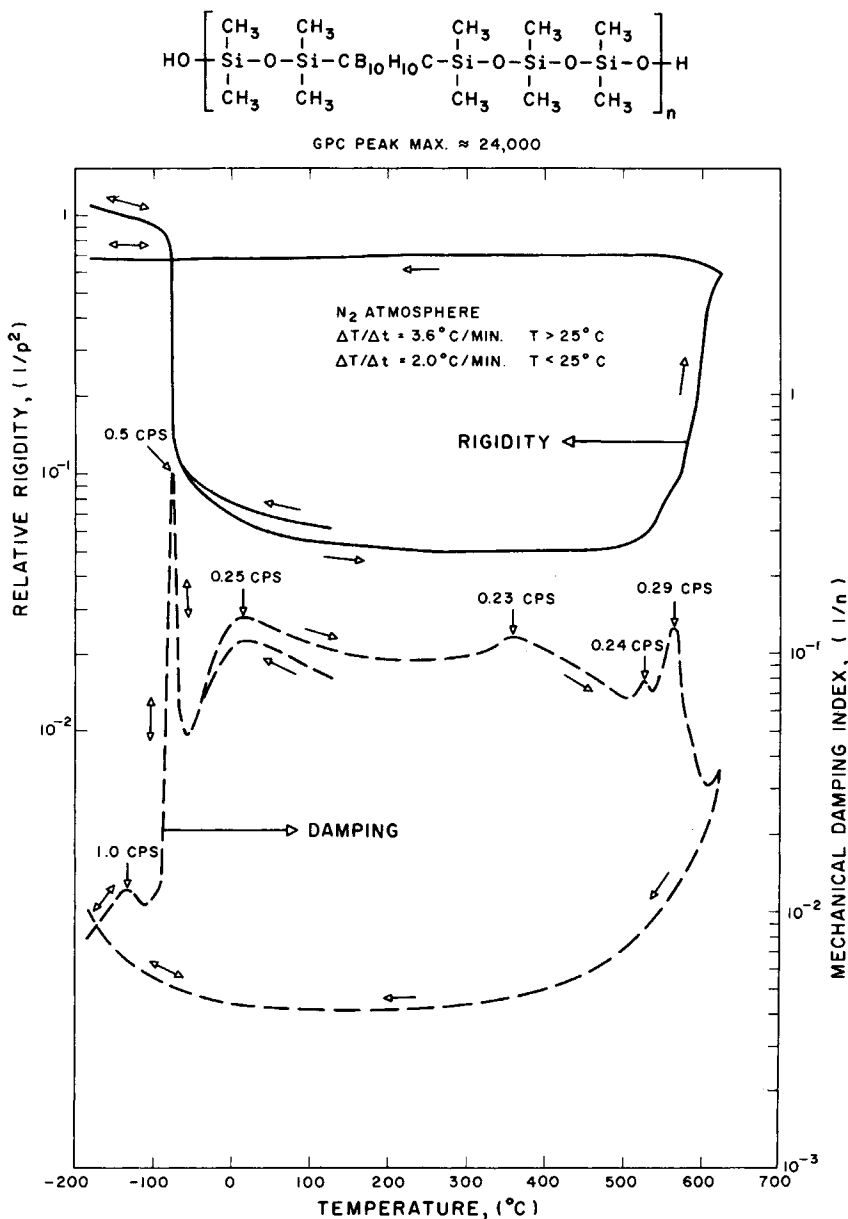
Fig. 7. 10-SiB-4: thermomechanical spectra in nitrogen $(\Delta T/\Delta t = 3.6\,°C/min,$ $T > 25°C;\ \Delta T/\Delta t = 2°C/min,\ T < 25°C)$ from 130° to −180° to 625° to −180° to 25°C.
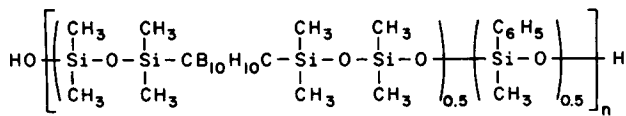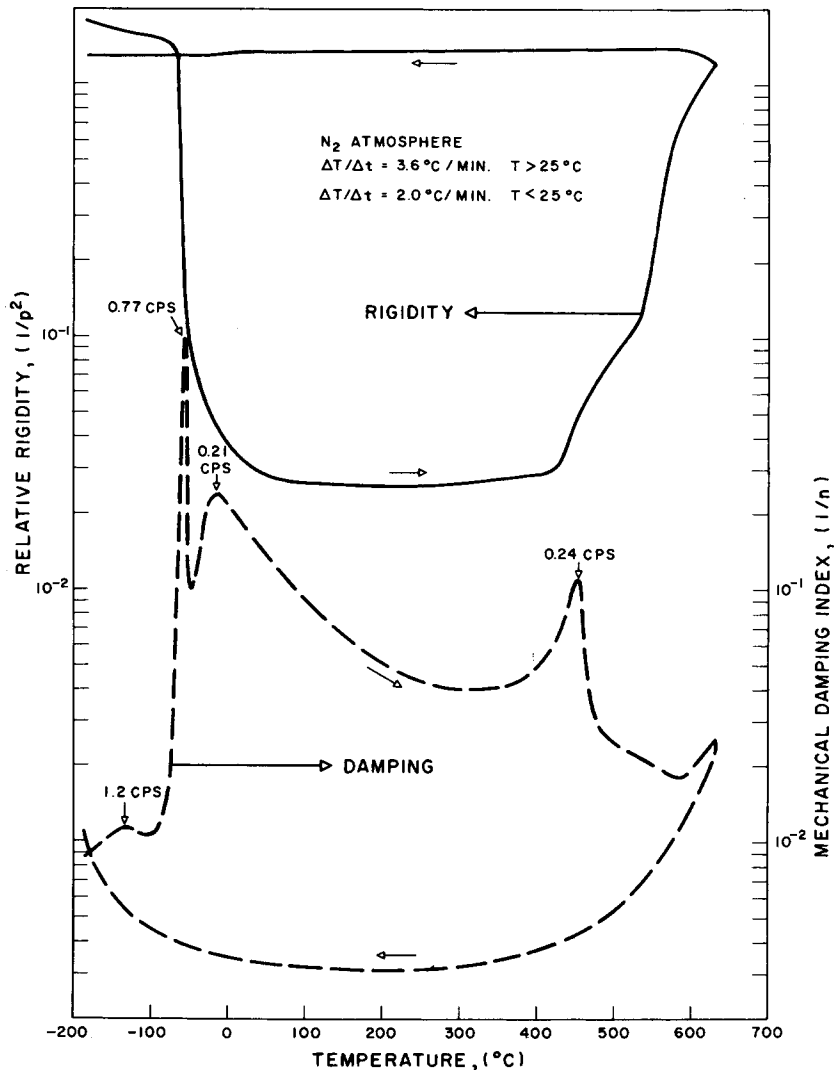
Fig. 8. 10-SiB-4 ϕ Random: thermomechanical spectra in nitrogen ($\Delta T/\Delta t$ = 3.6°C/min, $T > 25$°C; $\Delta T/\Delta t$ = 2°C/min, $T < 25$°C) from 130° to −180° to 625° to −180° to 25°C.

the bulk condensation of the dihydroxy monomer using tetramethylguan-
idine/sulfuric acid as catalyst:[5]

$$
\begin{array}{ccc}
CH_3 & CH_3 & \\
| & | & 170°C \\
HO\text{-}Si\text{-}CB_{10}H_{10}C\text{-} & Si\text{-}OH & \xrightarrow{\text{catalyst}} I + H_2O \\
| & | & \\
CH_3 & CH_3 &
\end{array}
$$
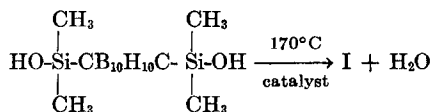
Polymer IV was prepared by the same procedure using the monomer

$$
\begin{array}{cccc}
CH_3 \ CH_3 & & CH_3 \ CH_3 \\
| \quad | & & | \quad | \\
HO\text{-}Si\text{-}O\text{-}Si\text{-}CB_{10}H_{10}C\text{-}Si\text{-}O\text{-}Si\text{-}OH. \\
| \quad | & & | \quad | \\
CH_3 \ CH_3 & & CH_3 \ CH_3
\end{array}
$$
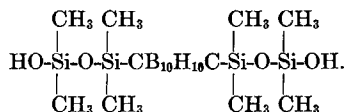
Polymer VI was prepared in a manner similar to IV using the dihydroxy
monomer which had one —CH_3 group on each silicon atom replaced by
—$C_2H_4CF_3$.[2]   The —$C_2H_4CF_3$ groups are expected to be placed atactically
along the chain.   Polymers VII, IX, and X were synthesized (in bulk)
by an initial dichloro–dihydroxy condensation to give a prepolymer, as
shown below[5,6]:

$$
\begin{array}{ccc}
CH_3 \ CH_3 & CH_3 \ CH_3 & R \\
| \quad | & | \quad | & | \\
nHO\text{-}Si\text{-}O\text{-}Si\text{-}CB_{10}H_{16}C\text{-}Si\text{-}O\text{-}Si\text{-}OH + nCl\text{-}Si\text{-}Cl \rightarrow \\
| \quad | & | \quad | & | \quad \Delta \\
CH_3 \ CH_3 & CH_3 \ CH_3 & CH_3
\end{array}
$$

$$
H\left[
\begin{array}{ccc}
CH_3 \ CH_3 & CH_3 \ CH_3 \ R \\
| \quad | & | \quad | \ | \\
O\text{-}Si\text{-}O\text{-}Si\text{-}CB_{10}H_{10}C\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-}Si\text{-} \\
| \quad | & | \quad | \ | \\
CH_3 \ CH_3 & CH_3 \ CH_3 \ CH_3
\end{array}
\right]Cl + nHCl
$$
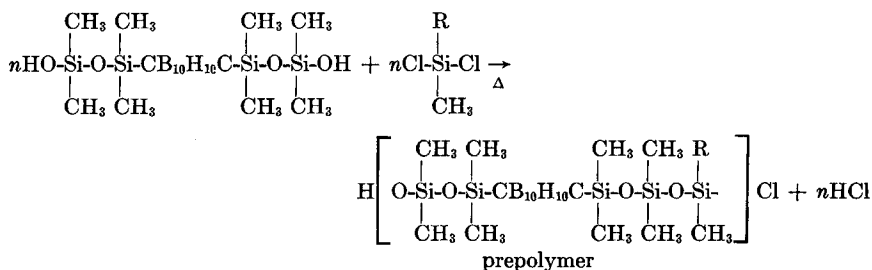
prepolymer

where R = —C_6H_5; —CH_3.   The prepolymer (GPC peak maximum 4000,
$n \sim 8$) was hydrolyzed and then reacted at elevated temperatures, using
tetramethylguanidine/sulfuric acid as catalyst, in aromatic hydrocarbon
solvents for R = —C_6H_5 and in bulk for R = —CH_3.[4,6]   As in the case of the
other substituted polymers (V and VI), the —C_6H_5 group is presumably
placed atactically in the chain.

The poor solubility of I (discussed in more detail later) resulted in the
polymer only being washed with hot xylene and water in its work-up.[6]
All the other polymer products were dissolved in ether, filtered, precipi-
tated with methanol, and dried in vacuo.[6]

Techniques

The thermomechanical data were generated under flowing dried "Hi-
Pure" nitrogen with the torsional braid apparatus (TBA).[7,8,9]   Thermo-
gravimetric analyses (TGA) and differential thermal analyses (DTA)
were performed in flowing argon with a du Pont 900 series thermoanalyzer
(the differential thermal analyses were run in a standard du Pont DSC
cell).
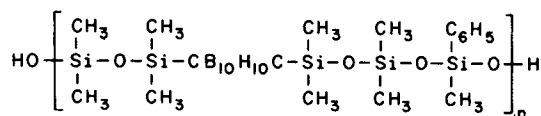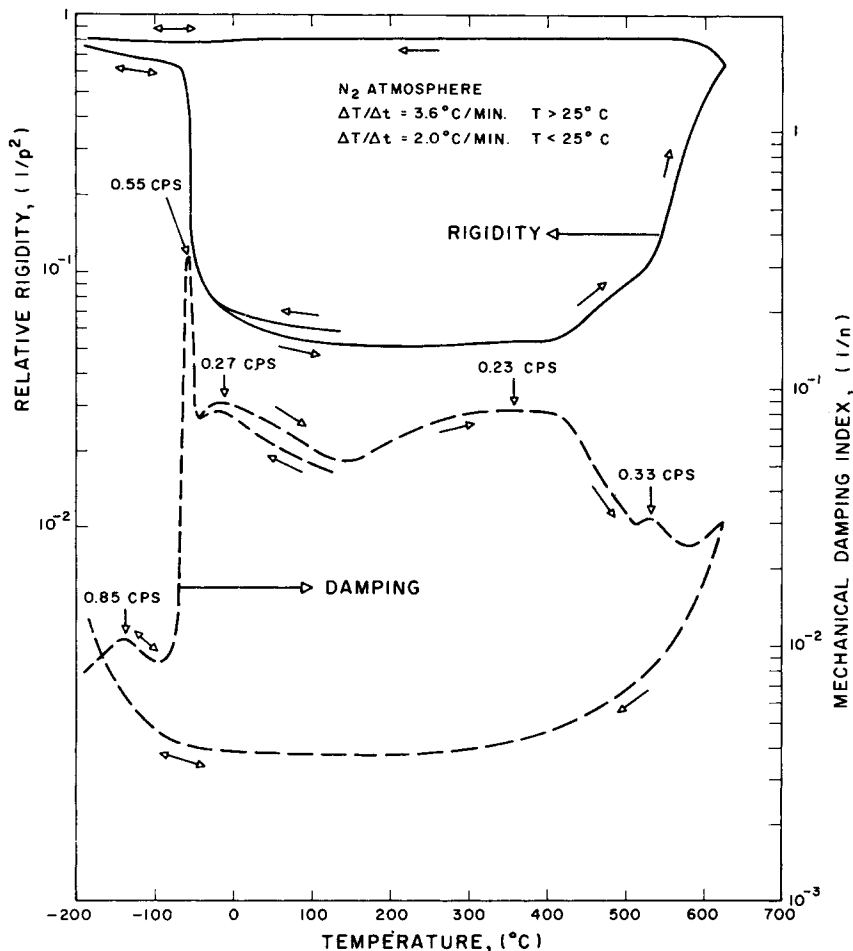
Fig. 9. 10-SiB-4 ϕ: thermomechanical spectra in nitrogen ($\Delta T/\Delta t$ = 3.6°C/min, $T > 25$°C; $\Delta T/\Delta t$ = 2°C/min, $T < 25$°C) from 130° to −180° to 625° to −180° to 25°C.

All the polymers, except I, are soluble in benzene; specimens were prepared from 10% (weight polymer/volume solvent) solutions. Polymer I formed a 5% gel in xylene at 25°C which became a slurry on refluxing (at about 140°C).

Each mechanical specimen was fabricated from a glass braid which was presoaked in benzene (xylene for I) before being immersed in the corre-
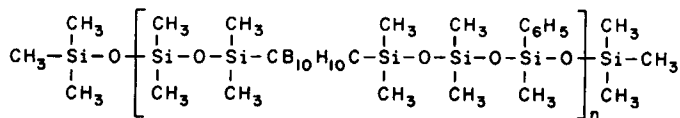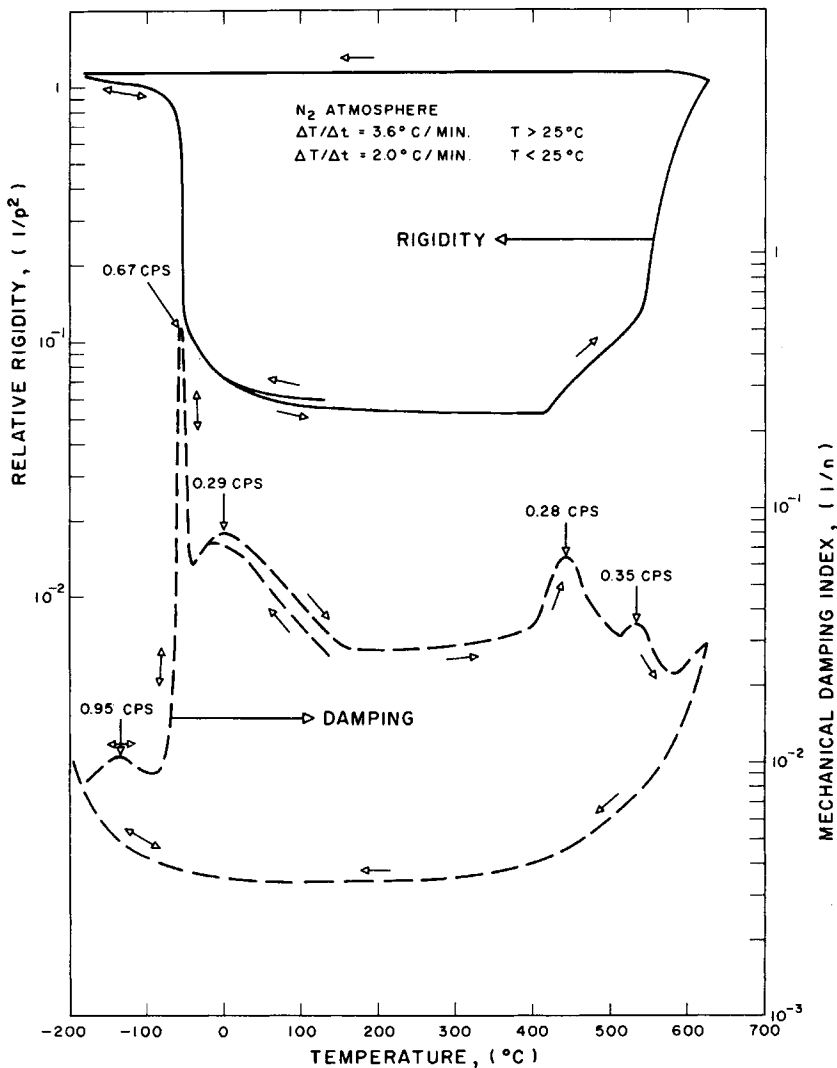
Fig. 10. 10-SiB-4 ϕ End-Capped: thermomechanical spectra in nitrogen ($\Delta T/\Delta t$ = 3.6°C/min, $T > 25$°C; $\Delta T/\Delta t$ = 2°C/min., $T < 25$°C) from 130° to −180° to 625° to −180° to 25°C.
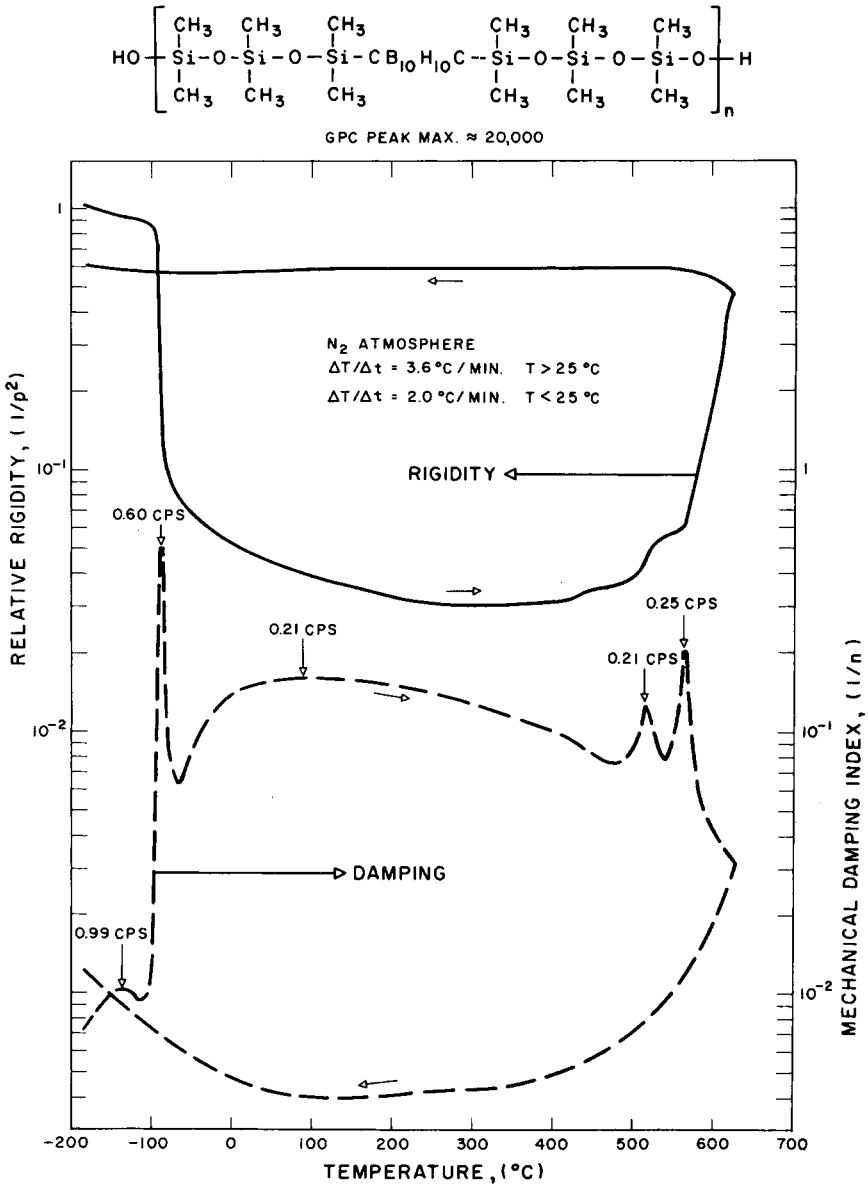
Fig. 11. 10-SiB-5: thermomechanical spectra in nitrogen ($\Delta T/\Delta t$ = 3.6°C/min, T > 25°C; $\Delta T/\Delta t$ = 2°C/min, T < 25°C) from 130° to −180° to 625° to −180° to 25°C.

sponding polymer solution or slurry (for I, refluxing under nitrogen) for ½ hr. In the case of I, after soaking the braid in the hot slurry, additional hot slurry was added with a medicine dropper. The benzene/polymer/glass composites were loaded into the TBA apparatus and were dried by heating at 2°C/min to 200°C in flowing, dried nitrogen. The
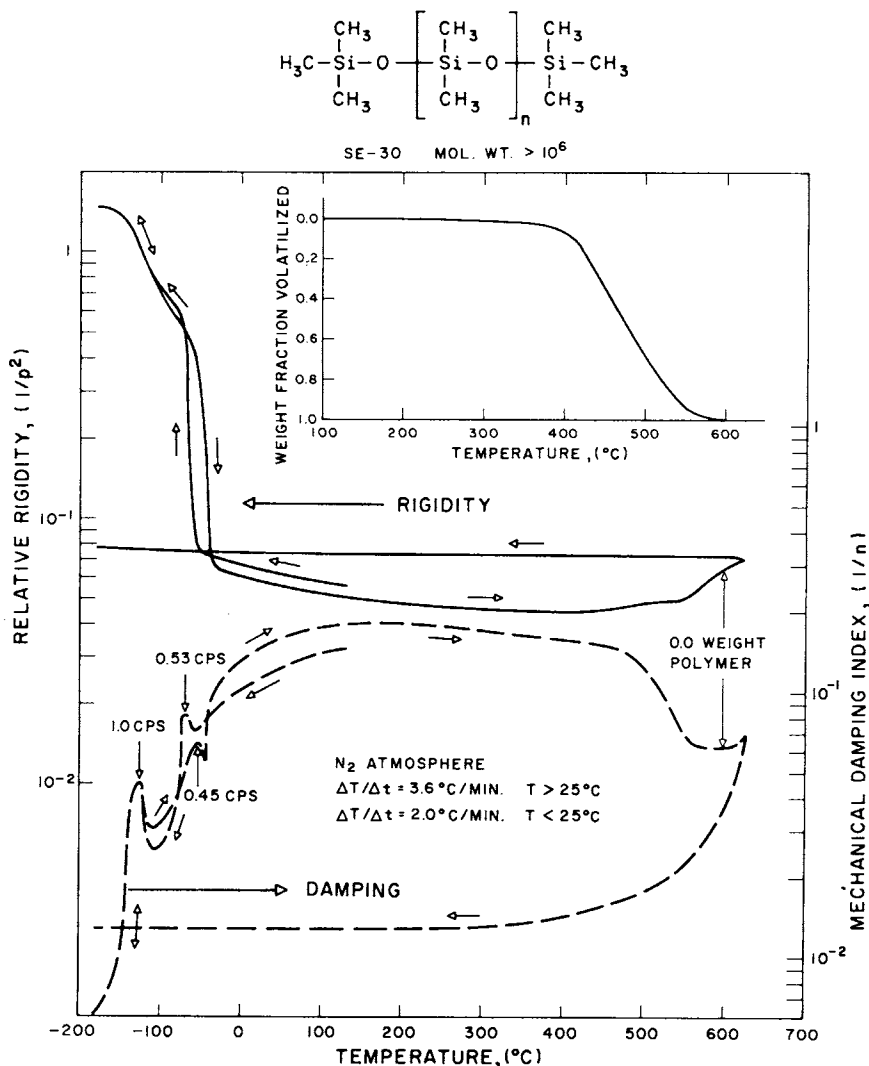
Fig. 12. 10-SiB-∞, SE-30: thermomechanical spectra in nitrogen ($\Delta T/\Delta t = 3.6°C/$ min, $T > 25°C$; $\Delta T/\Delta t = 2°C/min$, $T < 25°C$) from 130° to $-180°$ to 625° to $-180°$ to 25°C. Thermogravimetric analysis data (insert) in argon ($\Delta T/\Delta t = 3.6°C/min$).

solution casting and thermal pretreatment to above both T_g and T_m of the benzene-soluble polymers provided the basis for expecting good penetration by the polymer molecules into the braid. The slurry-cast xylene/polymer I/glass composite was dried by heating at 2°C/min to 280°C (under flowing nitrogen) in order to melt the polymer ($T_m = 260°C$). After drying, the specimens were stored overnight in the apparatus under flowing, dried nitrogen at 130°C. The following day, the data from 130°C to $-180°$C to 130°C at 2°C/min were taken. The specimens were again stored overnight at 130°C. On the third day, the specimens were taken

COPOLYMER EQUATION FOR 10-SiB-x POLYMERS

$$\left[\left(\begin{array}{c}CH_3 \\ | \\ -Si-CB_{10}H_{10}C \\ | \\ CH_3\end{array}\right)\left(\begin{array}{c}CH_3 \\ | \\ -Si-O \\ | \\ CH_3\end{array}\right)_x\right]_n$$

$$\frac{1}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} = W_1\left(\frac{1}{T_{g_1}} - \frac{1}{T_{g_2}}\right) + \frac{1}{T_{g_2}}$$

10-SiB-x	T_g (°K)	W_1
x = 1	298	0.73
x = 2	231	0.575
x = 3	205	0.475
x = 4	198	0.404
x = 5	185	0.351
x = ∞	148	0.0

−7°C EXTRAPOLATED FOR x=1

103 °C EXTRAPOLATED FOR T_{g_1}

W_1 = WEIGHT FRACTION $-Si(CH_3)_2 - CB_{10}H_{10}C-$
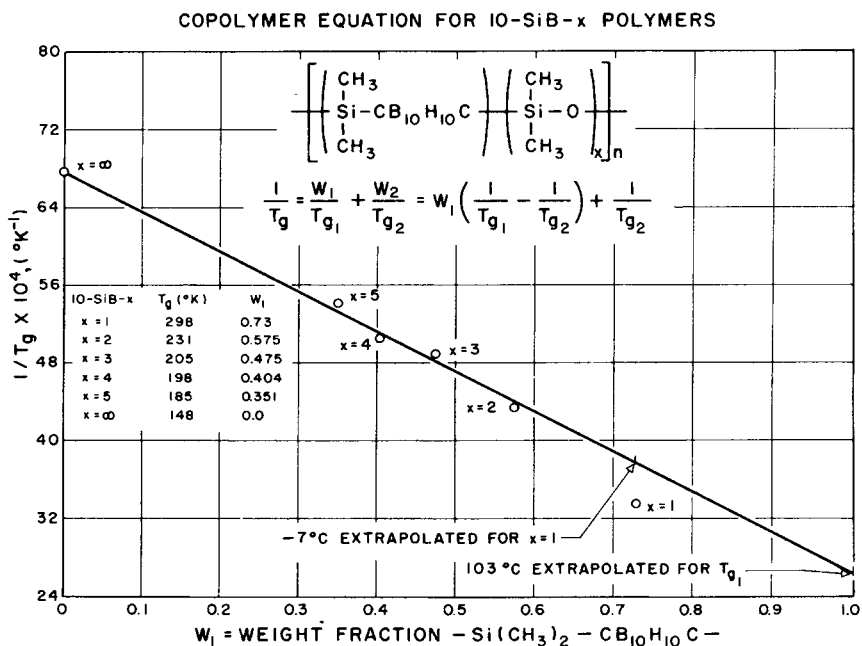
Fig. 13. 10-SiB-x polymers as copolymers of 10-SiB-0 and 10-SiB-∞ : glass transition temperature-structure correlation.

10-SiB-3 PARA (Ⅴ)

10-SiB-3 HIGH MW (Ⅳ)

10-SiB-3 (Ⅱ) &
10-SiB-3 END-CAPPED (Ⅲ)

10-SiB-3 FLUORINATED (Ⅵ)

ARGON ATMOSPHERE
ΔT/Δt = 3.6 °C/MIN.

WEIGHT FRACTION VOLATILIZED

TEMPERATURE, (°C)
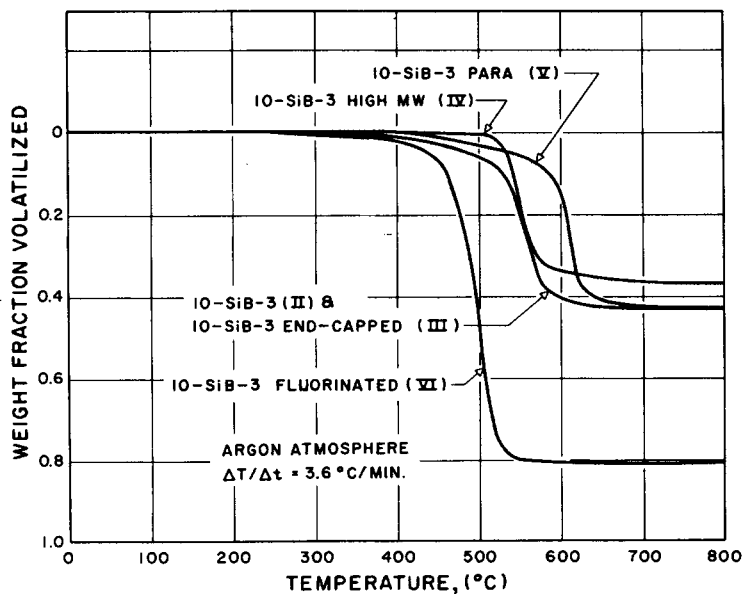
Fig. 14. 10-SiB-3 Polymers: thermogravimetric analysis in argon.
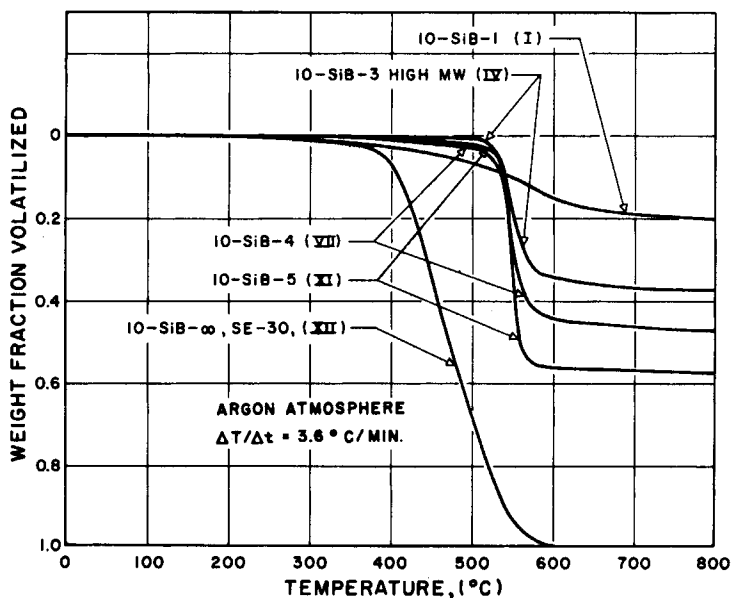
Fig. 15. 10-SiB-x Polymers: thermogravimetric analyses in argon.
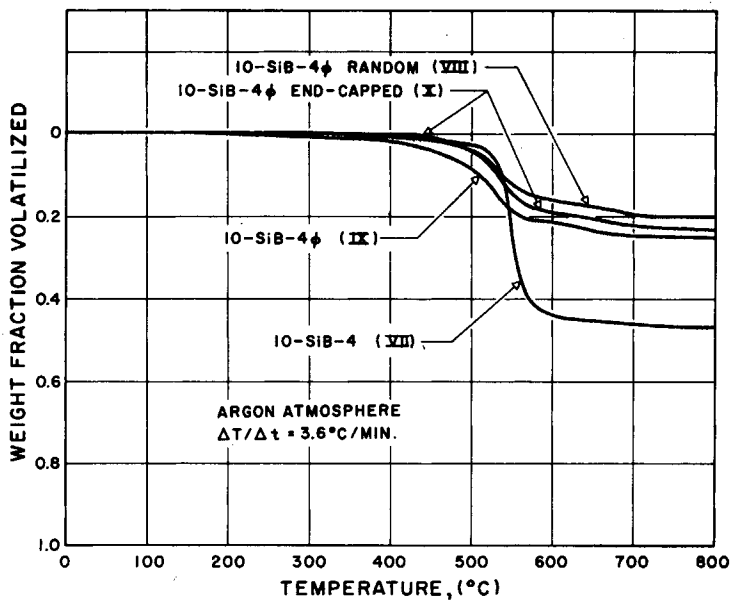
Fig. 16. 10-SiB-4 Polymers: thermogravimetric analyses in argon.

through the cycle 130°C to 625°C to 130°C at 3.6°C/min and then from 130°C to −180°C to 20°C at 2°C/min. The resulting thermomechanical spectra are presented in Figures 1–12. A glass transition-structure correlation which was derived from the thermomechanical spectra appears in Figure 13.
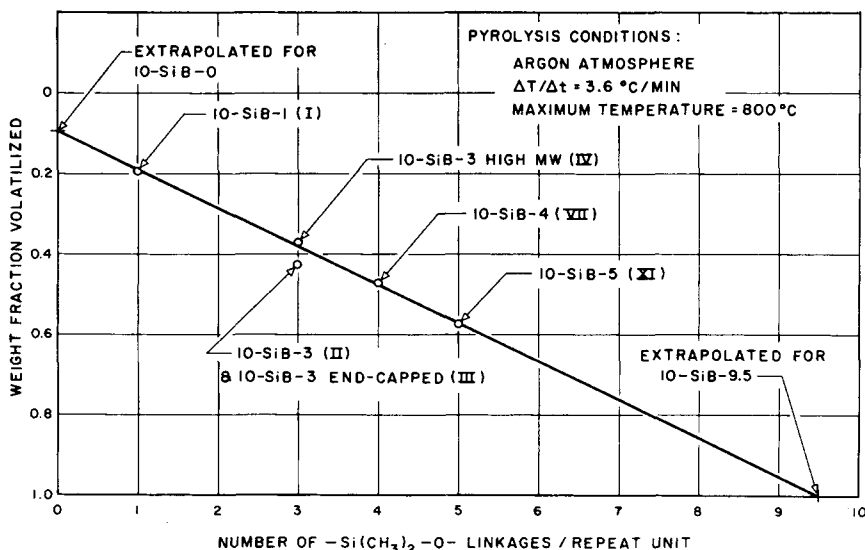
Fig. 17. 10-SiB-x Polymers: correlation between molecular structures and pyrolysis in argon. The weight fraction volatilized by heating to 800°C is plotted vs. the number of siloxane linkages per repeat unit.

Each specimen for the TGA experiments was dried from solution or gel (for polymer I) on the thermobalance at 2°C/min to 200°C in flowing argon, and then was run from 130°C to 800°C at 3.6°C/min in flowing argon in order to duplicate the heating program for the mechanical work. The results are presented in Figures 14–16. A weight loss-structure correlation which was derived from the thermograms appears in Figure 17.

The specimens for the DTA experiments were the "as received" polymers which were examined from 25° to 590°C at 15°C/min in flowing argon.

RESULTS AND DISCUSSION

Physical Transitions

Table I summarizes the transition data for the 10-SiB-x polymers as determined by TBA.

Variations of the 10-SiB-3 Structure (II–VI)

The thermomechanical data are shown in Figures 2–6. All the curves are line diagrams except that for polymer II, for which data points are shown in order to display typical scatter of the experimental data.

For the given backbone structure (i.e., 10-SiB-3), when the molecular weight is changed from about 10,000 to above 50,000, there appeared to be no effect (cf. II and IV), except for the absence of crystallinity in the high molecular weight polymer. There also appeared to be no effect when the

reactive endgroups are replaced by nonreactive endgroups (cf. II and III). All of the 10-SiB-3 polymers with *meta*-carborane and all-methyl side groups had glass transition temperatures (T_g) at about $-68°C$ and low-temperature transitions (T_{sec}) at $-140°C$ (note that the low-temperature damping peaks were accompanied by inflections in the rigidity curves). The two waxy polymers (II and III) had melting points (T_m) at $+40°C$. Polymers II and III crystallized at $+10°C$, and both displayed hysteresis between the glassy and melt regions on cooling and subsequent heating. Some of the amorphous polymers (IV, VII, IX, and X) displayed hysteresis above their glass transition temperatures. Replacement of the *meta*-carborane cage with the *para*-carborane cage (polymer V) raised T_m to $110°C$, T_g to $-35°C$, T_{sec} to $-115°C$, and T_{crys} to $90°C$. This may have been due to the effect of the less kinked nature of the molecule on the intermolecular packing of the chains. The *para*-carborane 10-SiB-3 displayed a higher degree of thermomechanical hysteresis than did the *meta*-10-SiB-3; the separation in the damping curve began at $-160°C$ in the glassy state, whereas in the rigidity curve it commenced near T_g. Hysteresis would be expected above the glass transition temperature for semicrystalline materials, even with a homogeneous specimen, since the thermomechanical experiment monitors a kinetic phenomenon under a dynamic temperature environment and equilibrium is not achieved. The hysteresis observed in the glassy state is probably a property of the composite nature of the crystalline polymer/braid specimen (e.g., microcracking).

Another variation in the 10-SiB-3 structure was the replacement of one —CH₃ group on each silicon atom with —C₂H₄CF₃ (VI). Although the molecular weight ($\sim$8500) of the material is somewhat low, certain trends in the effect of this variation were apparent. The T_g was raised $53°C$, from $-68°C$ for the dimethyl polymer, to $-15°C$ for the trifluoropropyl polymer. If the effect of molecular weight were to be observed, T_g would be even higher than $-15°C$ for higher molecular weights. Above the glass transition temperature, at about $50°C$, the large, broad damping peak corresponded to a large, broad drop in rigidity which is characteristic of flow. The low-temperature secondary transition had disappeared, or had possibly been shifted up to $-90°C$ where it may have manifested itself as a small shoulder in the low-temperature tail of the T_g peak. There was also a significant rise in damping below $-100°C$ which diagnosed a further mode of submolecular motion. This rise has been observed in this laboratory for a 5-SiB-1 material, containing —CB₅H₅C— cages, similarly substituted with trifluoropropyl groups.[15] This relaxation may have been undetected in the other polymers which have been examined herein due to the low-temperature limitation ($-180°C$) of the apparatus and may have appeared in this case as the result of a general shift of the transitions to higher temperatures caused by the presence of —C₂H₄CF₃ groups. On the other hand, it may be related to the onset of motion of the —C₂H₄CF₃ groups *per se*. Motion of this type has been reported for the poly(*n*-alkylmethacrylate) polymers with *n*-propyl and *n*-butyl groups.[10,11]

Polymer VI displayed hysteresis in the rigidity data that increased with increasing residence time at low temperatures (the turn-around time was not always reproducible). The phenomenon may have been a composite property related to the formation of microcracks which can be caused by thermal stresses arising from differences in thermal coefficients of expansion of the two components of the composite specimen. The hysteresis loop closed as the temperature approached the glass transition temperature, indicating that a "healing" process occurred. The irreversibility may also have arisen from an inherent brittleness due to the low molecular weight, or may be related to the freezing out of energy-absorbing submolecular motions which are associated with the increase in damping below $-100°C$. It might also be of relevance that the polymer displayed unusually high adhesion to glass. It is of interest to note that the damping did not appear to reflect the irreversibility of the rigidity. This was probably due to the rapid changes in molecular friction (i.e., damping) occurring in this temperature range which overshadowed the effect of microcracking.

In-Chain Variations in the 10-SiB-x Structure
(I, IV, VII, XI, and XII)

The thermomechanical data of polymers in the 10-SiB-x series, where $x = 1, 3, 4, 5, \infty$ [∞ corresponds to pure poly(dimethylsiloxane)], are presented in Figures 1–4, 7, 11, and 12. The corresponding glass transition temperatures are $25°$, $-68°$, $-75°$, $-88°$, and $-125°C$, respectively. For $x = 3, 4$, and 5, there was a secondary transition in the vicinity of $-135°$ to $-140°C$. 10-SiB-1 had a T_{sec} at $-90°C$, while 10-SiB-∞ displayed no apparent secondary transition above $-180°C$ (this may have been due to the low value of the glass transition resulting in a merging of the large T_g peak and a smaller secondary peak). For $x = \infty$ ($T_m = -40°C$), the polymer was crystalline. For $x = 3$ ($T_m = 40°C$), the polymer was either amorphous (IV) or slightly crystalline (II and III, see above).

Figure 13 shows a plot of $1/T_g$ versus $W(1)$ [$W(1)$ = weight fraction of $-Si(CH_3)_2-CB_{10}H_{10}C-$ in the polymer repeat unit].[12] If the empirical copolymer equation[13,14]

$$1/T_g = W(1)/T_g(1) + W(2)/T_g(2)$$

can be applied to this alternating copolymer system [where the subscript 1 refers to $\{-Si(CH_3)_2-CB_{10}H_{10}C-\}$ and the subscript 2 refers to $\{-Si(CH_3)_2-O-\}_x$], the data should fall on a straight line. The $x = 3, 4, 5, \infty$ data fall well on a straight line. (The value for the $x = 2$ point was determined in this laboratory[15] using a recently synthesized linear 10-SiB-2 polymer of well-defined regular structure.[16] Data obtained by different techniques[17] on crosslinked polymer with overall structure 10-SiB-2[18] have been reported but do not fit the correlation as well.[12] The T_g of 10-SiB-1 polymer deviates from the trend established for the $x = 2$, $3, 4, 5, \infty$ polymers. The value $T_g = -7°C$ extrapolated from the straight

line is 32°C lower than the value $T_g = 25°C$ determined mechanically herein and also previously reported for cured and filled 10-SiB-1.[19] The unusually high T_g is accompanied by a value for T_{sec} of $-90°C$ which is high compared to values of T_{sec} of about $-140°C$ which have been obtained for all the other m-10-SiB-x polymers (and for several 5-SiB-x polymers containing $-CB_5H_5C-$ cages with the carbon atoms in the nonapex meta position, which have also been studied in this laboratory[12,20]). The T_m/T_g ratio of 1.78 (see Table I) for 10-SiB-1 is also out of line with the other 10-SiB-x polymers and even the highly symmetrical 10-SiB-∞ [poly(dimethylsiloxane)] the values for which lie in the range of 1.54–1.61.

The relatively high glass transition temperature of 10-SiB-1 is of interest. The "ball and chain" configuration of the 10-SiB-x polymers raises the question as to whether the bulk solid state properties are at some decreasing siloxane segment length dominated by the impingement of the balls on each other rather than being dominated by the linear macromolecular structure of the individual molecules. It has been suggested[12] that packing of carborane cages may be a major determinant of properties for the 10-SiB-1 polymer.

Carrying the extrapolation of the copolymer equation one step further, a T_g of 103°C is predicted for $(-Si(CH_3)_2-CB_{10}H_{10}C-)_n$ in the absence of any complicating factors. This value of the glass transition temperature appears to be low when the size of the carborane cage is considered (comparable to the volume that would be swept out by a benzene molecule spinning on a twofold axis). The character of the Si–C (carborane) bond is unusual in that the energy barriers for oscillation must be low in spite of the large size of the carborane cage.

It is also of interest to note that the copolymer equation which has been applied successfully to the 10-SiB-x series (and even more successfully to a 5-SiB-x series[12] from $x = \infty$ to $x = 1$) was proposed as being applicable to both diluent and copolymer systems.[13] However, various mixtures of polymers from the 10-SiB-X series (and the 5-SiB-x series) showed complete immiscibility.[21] The thermomechanical spectra of the mixtures displayed the transition temperatures of the individual components. This supports the notion of carborane cage aggregation which was invoked[12] to explain the anomalous behavior of the transitions of 10-SiB-1.

Variations of the 10-SiB-4 Structures (VII–X)

The thermomechanical data are shown in Figures 7–10. Four 10-SiB-4 polymers were studied: the basic 10-SiB-4 (VII) all-methyl-substituted polymer; two 10-SiB-4 polymers (IX and X) of regular structure with the center silicon atom having one pendent phenyl group, one end-capped (X) and one with hydroxy endgroups (IX); one nonregularly structured 10-SiB-4 with 20% of the silicon atoms having one methyl group replaced by a phenyl group (VIII).

The transition data are presented in Table I. All four materials have a T_{sec} near $-140°C$ (a damping peak accompanied by an inflection in the rigidity curve). The basic 10-SiB-4 has a T_g of $-75°C$ (as discussed

above), and all three phenyl-substituted polymers have T_g values at about $-57°C$. Replacing 10% of the pendent methyl groups with the more bulky phenyl group caused an increase of about 18°C in the value of the glass transition temperature. With respect to the three phenylated polymers, there appeared to be no detectable differences in the low-temperature thermomechanical behavior of the nonregular, the regular, and the end-capped regular polymers. Therefore, the nonregular structure must be a random copolymer and not a mixture of poly(methylphenylsiloxane) and polymer 10-SiB-3 nor a block copolymer. The immiscibility of the seemingly similar 10-SiB and silicone polymers[21] would lead to two independent glass transitions for both mixtures and block copolymers.

Thermal Stability

Thermogravimetric analyses (TGA) in argon for the three groups of polymers discussed above are shown in Figures 14, 15, and 16.

Variations in the 10-SiB-3 Structure (II–VI)

It can be seen that in terms of the temperature where the maximum rate of weight loss occurred, V was the most stable (about 610°C); II, III, and IV were next (about 560°C), and VI was the least stable (about 490°C). In terms of the final per cent weight retained at 800°C, IV was most stable (62%); II, III, and V were next (57%), and VI was again the least stable (19%). The high molecular weight 10-SiB-3 (IV) began to lose weight at a higher temperature than did II, III, and VI. The 5% difference in 800°C retained weight (IV versus II and III) could well have been due to the loss of low molecular weight volatiles and not be indicative of the true stability of the materials, since the data were relatively parallel (5% spread) from 500° to 800°C. This, of course, was not the case for VI, where approximately 60% by weight of the repeat unit was organic side groups ($—C_2H_4CF_3$), compared to approximately 27% for the totally methylated II, III, and IV. It is also of interest to note that although the weight loss at 800°C does not correspond to the weight per cent of organic side groups, the ratio of weight losses is approximately equal to the ratio of organic weight fractions (i.e., 2:1). The equivalence of the weight loss by 800°C of II, III, and V is perplexing if weight loss is due to the formation of volatile cyclics, as is the case for pure silicones[22–24] and as might be expected from the cyclic nature of the polymerization byproducts.[3] The *meta*-carborane linkages cause kinks in the chain and could be expected to aid cyclization relative to *para*-carborane linkages where the colinear bonds would tend to retard ring formation.

In-Chain Variations in the 10-SiB-x Structure (I, IV, VII, XI, and XII)

Figure 15 shows that as the length of the $—Si(CH_3)_2—O—$ chain sequence increased, the final weight retained by 800°C decreased to the limit of total depolymerization for pure poly(dimethylsiloxane) (XII). It is also interesting to note that all of the materials containing the *meta*-carborane cage experienced the largest rate of weight loss in the range of 500–560°C.

(The broadness of this region for 10-SiB-1 polymer (I) made its temperature of maximum weight loss difficult to pinpoint.) The maximum rate of weight loss was at about 475°C for the pure silicone. A plot of final weight retained by 800°C versus the number of —Si(CH$_3$)$_2$—O— groups per repeat unit (Fig. 17) is a straight line which extrapolates to 10% weight loss for 10-SiB-0 and 100% weight loss for 10-SiB-9.5 (and presumably above). This relationship, coupled with the fact that there was only one weight loss region for all of these polymers, would again seem to discount the cyclization mechanism which would be expected to be optimal for some particular siloxane chain length as opposed to the monotonic nature of the data.

Variations in the 10-SiB-4 Structure (VII–X)

Figure 16 shows that a substitution of 10 mole-% of —C$_6$H$_5$ for —CH$_3$ resulted in a considerable decrease in the weight loss of VIII, IX, and X in comparison with totally methylated VII. The 5% weight loss spread of the data for the three phenylated materials is of interest. Most of the deviation occurred below 475°C, after which the plots became essentially parallel, with identical decreases and flat regions. The largest rate of weight loss occurred at approximately 550°C for VII and 530°C for the phenylated polymers VIII, IX, and X. The differences between VIII and both IX and X may be the result of the random versus defined nature of the structures. More likely, variations among all three would be expected to be due to differences in the molecular weight distributions resulting from different mechanisms of synthesis (VIII versus IX and X) or from different amounts of low ends which remained after the work-up procedures.

Differential thermal analyses (DTA) in argon and nitrogen were obtained at 15°C/min for specimens of 10-SiB-1 (I) and 10-SiB-4 ϕ (IX). These polymers were studied because the mechanical data (discussed later) indicated that these materials were the first to stiffen. In the case of 10-SiB-1, the only thermal event evident above room temperature was melting, with T_m = 250°C. Above 250°C, the plot (not shown) was virtually flat until 550°C, where a small broad endotherm began (this corresponded to the weight loss region). The endotherm peaked at 582°C. In the case of 10-SiB-4 ϕ, there was no character to the plot except for a small broad endotherm above 550°C similar to that observed with 10-SiB-1. Both specimens were brittle, discolored discs after the DTA runs. DTA data below 600°C in inert atmospheres seemed to add little to the study of the thermal stability of the 10-SiB polymers.

Thermomechanical Stability

Variations in the 10-SiB-3 Structure (II–VI)

The thermomechanical spectra are presented in Figures 2–6. The lower molecular weight meta-10-SiB-3 materials (II and III) gave identical spectra, indicating that reactive versus inert endgroups play no active role in the

degradation mechanism for the temperature program of this study. On heating, both polymers had a damping increase near 400°C and damping peaks at 570°C and 600°C and displayed catastrophic thermal stiffening (presumably due to crosslinking) commencing at 560°C. The high molecular weight polymer (IV) displayed a higher degree of damping which is indicative of a more viscous fluid; this tends to mask the damping peaks seen for II and III in the reaction region. Polymer IV also experienced catastrophic stiffening near 555°C. The small rises in rigidity which occurred between 350°C and 550°C are more difficult to interpret and may have been due to weight loss commencing in this region or the increased effect of the rigidity of the glass braid as the polymer viscosity decreased. On cooling from 625°C, all three polymers appeared to act as highly crosslinked rubbers. After the initial 25°C of cooling (during which the reaction may have been continuing), the rigidity curve had a positive coefficient of rigidity as a function of temperature until the 50–100°C range where the rigidity began to increase with decreasing temperature. This decrease in rigidity with decreasing temperature (above T_g) is a key feature predicted by the theory of ideal rubber elasticity. The corresponding very low level of damping which was experienced is also in line with the hypothesis of an ideally elastic rubber. The increase in damping below about 300°C and the increase in rigidity below 50°C indicated a very broad glass transition region commencing about 0°C for the pyrolyzed (to 625°C) polymers. Previously reported work[19] has shown that crosslinked 10-SiB-2 and 10-SiB-1.5 display temperature-dependent elastomeric properties above T_m.

The fourth 10-SiB-3 polymer (V) contains the *para*-carborane cage in its backbone. The *para*-carborane cage might be expected to stabilize the polymer since the less kinked nature of the molecule would render the formation of low molecular weight cyclics more difficult (cyclic product formation is the major mode of thermal decomposition of classical silicone polymers[22-24]). This stabilization effect appeared to be active with respect to weight loss (cf. the 50°C higher temperature for the maximum rate of weight loss for V versus the corresponding temperatures for II, III, and IV). Thermomechanically, there seemed to be a little additional stability above 370°C for polymer V, as evidenced by a damping peak at 610°C as opposed to 600°C for II and III, and catastrophic stiffening starting near 570°C rather than 560°C. On the other hand, solubility studies indicated a lower gel temperature for the *para*-versus *meta*-carborane polymers (see below). With this in mind, closer examination of the relative rigidity curve for 10-SiB-3 para (V) revealed a small step-increase in stiffness at about 400°C. The corresponding *meta*-10-SiB-3 polymers (II, III, and IV) displayed no such increase in rigidity until temperatures greater than 500°C. On cooling from 625°C, the material behavior appeared to be very much like that of II, III, and IV. The rigidity curves of II, III, IV, and V are virtually superimposable from 570°C to 625°C to −180°C.

The last of the 10-SiB-3 polymers to be considered is VI, which has one methyl group on each silicon atom replaced by a 1,1,1-trifluoropropyl group. This polymer, having a larger organic content than the other

10-SiB-3 polymers, would be expected to be less thermally stable due to the breakdown of the organic side groups. The confirmation of this with respect to TGA has been discussed. The same conclusion can be drawn from the thermomechanical spectra. A damping peak at 490°C, accompanied by the onset of catastrophic stiffening, occurred at approximately 480°C. The stiffening appeared to be two-staged. The first from 480°C to 510°C and the second from 510°C to 625°C. The onset of the second stage corresponded to a 515°C minimum in the damping. On cooling, the rigidity of the pyrolyzed polymer rose to a high, flat level and the damping dropped to a low, relatively constant level. This is the behavior of a highly crosslinked resin, and these features are prominent even though 80% of the weight of the original polymer, as monitored by TGA, is lost by 550°C.

Other experiments have shown[25] that reducing the rate of temperature rise to 2.0–3.0°C/min results in material behavior (after pyrolysis) of II, III, IV, and V, basically similar to that of VI presented here (at 3.6°C/ min), which is indicative of a lack of elastomeric behavior.

After the thermomechanical experiments, all the 10-SiB-3 specimens were water-white, stiff rods (the individual fibers of the support braid were visible), except the fluorinated polymer which had blackened somewhat and was opaque.

In-Chain Variations in the 10-SiB-x Structure
(I, II, III, IV, VII, XI, and XII)

The thermomechanical spectra are presented in Figures 1, 2–4, 7, 11, and 12. A priori, the thermomechanical stability might be expected to be a monotonically varying function from $x = 1$ to $x = \infty$ (or some approximation of ∞; cf. $x = 10$ for TGA data), as was seen for the weight loss data (at 800°C). Analysis of the data shows that this is not the case.

Polymer I experienced an increase in rigidity commencing at 380°C which was accompanied by a broad, flat damping peak. A more catastrophic increase in rigidity began at about 545°C with a corresponding damping peak (550°C). At 580°C, the rate of stiffening increased again. On cooling from 625°C, the material displayed properties that are common to highly crosslinked resins (high, flat rigidity–temperature curve and low damping). Again, it is necessary to repeat that the nature of the particular 10-SiB-1 polymer is such that the purity of the material (with respect to catalyst residue and other foreign matter, not as related to polymer structure) is uncertain. Catalyst residues and other foreign matter can, at elevated temperatures, initiate polymer degradation via depolymerization, chain stiffening, or crosslinking. This may or may not have occurred in the vicinity of 380°C for polymer I.

Polymers II, III, and IV were discussed above in considering the 10-SiB-3 series. The important features which are pertinent to the 10-SiB-x series are: (1) the small increase in rigidity near 510°C; (2) the catastrophic increase in rigidity above 560°C, and (3) the elastomeric character of the material on cooling from 625°C.

Polymer VII, 10-SiB-4, had high-temperature thermal properties that appeared to be similar to those of II, III, and IV. There were two high-temperature damping peaks at 530°C and 570°C (570°C and 600°C for II and III) which would indicate a lower threshold temperature for thermal reaction. The rigidity began to increase significantly above 530°C and then catastrophically at 560°C. On cooling from 625°C, the material behaved as a highly crosslinked resin, in contrast to the crosslinked elastomers from the 10-SiB-3 series (II, III, and IV).

Polymer XI, 10-SiB-5, displayed features basic to others in the series (II, III, IV, and VII). There were, again, two high-temperature damping peaks at 515°C and 565°C. The rigidity correspondingly experienced an increase near 510°C and then the typical catastrophic stiffening at 560°C. On cooling, XI was like I and VII, a highly crosslinked resin.

The last material in this series, XII, 10-SiB-∞, is a commercial, unvulcanized gum silicone rubber (SE-30). The TGA data showed that, by about 600°C, the polymer had completely depolymerized (to form volatile low molecular weight cyclics). The high-temperature thermomechanical behavior of XII reflected this. The rigidity remained at a constant low level until 400°C where a gentle upward slope began corresponding to the onset of catastrophic weight loss. At 550°C, where less than 10% of the polymer remained, the rigidity began to rise more rapidly. When the amount of material on the braid becomes small enough, the period of oscillation (P) should reflect more the properties of the glass braid substrate.

The damping was high at room temperature and above for polymer XII, by virtue of the high molecular weight of the material (>1,000,000), and therefore masked any peaks due to the reactions associated with depolymerization. The damping began to decrease at about 450°C, which corresponded to a 35% total weight loss. This decrease was probably related to the decrease in viscous character of the material corresponding to the decrease in molecular weight as a result of depolymerization. At 550°C, the damping leveled off. On cooling from 625°C, the rigidity was very low relative to both the glassy state of XII and the other materials studied, and was absolutely flat. The damping fell off to a constant but relatively high level compared to the other materials ($1/n = 0.013$ for XII, compared to 0.004 for several of the others). The braid, after being removed from the TBA, was clean and flexible, like an unused braid. The other specimens were colorless, clear, stiff rods as discussed for the 10-SiB-3 series, except for I (10-SiB-1) which remained clear but had darkened to black-brown along its length.

The data for polymer XII (Fig. 12) are of special interest since they provide information on how the composite responds to weight loss and on the temperature dependence of the glass braid substrate itself after thermal treatment to 625°C. The low degree of mechanical response to weight losses in excess of 50% for fluid polymers points out the need to correlate TBA data with the results of TGA and other techniques. On the other hand,

the high rigidity level displayed by all the polymers discussed (except XII) is indeed a polymer or resin property. On cooling from 625°C after pyrolysis the damping does, to some extent, reflect the properties of the supporting glass, but this is a monotonic decrease with decreasing temperature to a flat level below about 400°C. The lower damping level observed for most polymers and the elastomeric effect observed in various 10-SiB-3 polymers after pyrolysis must be attributed to the polymers themselves.

Thermomechanically, the 10-SiB-x polymers (I, II, III, IV, VII, XI, and XII) do tend to follow the stability trend determined by TGA, with the exception of 10-SiB-1 which is mechanically the least stable.

The low weight loss observed for 10-SiB-1 may be related to a chain scission which would generate active species and not lead to the formation of cyclic volatiles but rather to the propagation of crosslinks. This scission and subsequent stiffening may be the result of catalyst residue impurities (see discussion above).

In the $x = 3$ polymers, (II, III, and IV), an optimum is reached which brings the threshold of mechanical stability to approximately 560°C, which is a temperature region at which all the materials discussed thus far (except VI), and those still to be discussed, displayed a stiffening mechanism. It would appear that this is the limit of mechanical stability. The $x = 4$ (VII) and $x = 5$ (XI) polymers each appear to crosslink at lower temperatures; due to its total weight loss, XII ($x = \infty$) is, of course, not thermomechanically stable. A solubility test was run on II, III, IV, V, VII, IX, XI, and XII. The experiment was to heat the eight weighed specimens of the polymers, held in uncoated DTA pans in the DSC oven, at 3.6°C/min to 500°C under flowing argon and then to cool quickly. The pans with the previously heated polymers were weighed (the retained weights were in close agreement with the TGA results) and then placed in a large amount of benzene and left overnight to dissolve or swell. They were then dried in a vacuum oven at 45°C overnight and weighed again. All the meta-10-SiB-3 (II, III, and IV) samples dissolved, leaving at most a 2.5% swelled residue. 10-SiB-4 (VII) swelled to the point of leaving about 17% of the postheating weight behind after extraction. 10-SiB-5 (XI) retained approximately 10% of its post heating weight after extraction. 10-SiB-4 ϕ (IX) appeared as several fragmented pieces of a disc that had not adhered to the pan, indicating, by the well-defined shape and low adhesion, a high degree of crosslinking. Another heating cycle, to 425°C, was performed on 10-SiB-4 ϕ, and 35% was found to remain after extraction. The 10-SiB-∞ (XII) retained less than 5% of its postheating weight, indicating that only a very small degree of crosslinking side reactions occurred during the depolymerization process. Para-10-SiB-3(V) retained 29% of its postheating weight after extraction, indicating a lower degree of stability, with respect to crosslinking, than any of the totally methylated meta-10-SiB-x polymers. After heating to only 425°C, the para-10-SiB-3 retained 7% of its postheating weight after extraction.

Variations in the 10-SiB-4 Structure (VII-X)

Mechanical data related to these polymers are shown in Figures 7–10. 10-SiB-4 (VII) was discussed above. The important features of the data for VII are that stiffening commenced between 500°C and 530°C and catastrophic stiffening occurred near 570°C. The other polymers (VIII, IX, and X) displayed differences in damping that would be expected to be related to differences in molecular weight or molecular weight distribution (see discussion under TGA results). The damping data for IX relative to that for VIII and X was what might be expected if there was an energy-dissipating phenomenon occurring such as vaporization of low molecular weight material, as seen (for IX) by TGA, which is characterized by such a phenomenon. The 530°C damping peak which was apparent for IX and X appeared as a shoulder for VIII. The 430°C peak in the spectra for VIII and X appeared as a skewed decrease in damping for IX. The rigidity curves for VIII, IX, and X were identical in shape, if not magnitude (geometry dependence of specimens). The rigidity curve was flat until 430°C, when a sharp rise began. At 550°C, a second stage of stiffening began. On cooling from 625°C, the materials all displayed behavior typical of highly crosslinked resins. The 430°C rise in rigidity, resulting from either chain stiffening or crosslinking, lends some understanding to the lower total weight loss of the 10-SiB-4 ϕ (VIII, IX, and X) polymers as compared to that of the 10-SiB-4 (VII) polymer. A crosslinked material would be expected to lose less weight than a linear material of similar chemical structure, since several bond breakages, rather than one, are necessary to free a low molecular weight species. This same effect seems to have been operative, with respect to weight loss, in the cases of 10-SiB-3 para (V) and 10-SiB-1 (I). Although the thermomechanical spectra of the end-capped and unend-capped 10-SiB-4 polymers (IX and X) were similar, a solubility study on preheated specimens (3.6°C/min in nitrogen to 400°C) showed that more crosslinking occurred with the hydroxy-terminated polymer. The ratio of the gelled fractions was about 3/1.

A recently published review on carborane polymers[26] reports a mechanism of crosslinking for the modified, low molecular weight phenylated 10-SiB-2 polymer which was alluded to in the introduction of this report. The polymer has the structure

$$HO—[—Si(CH_3)_2—CB_{10}H_{10}C—Si(CH_3)_2—O—Si(C_6H_5)\ (CH_3)—O—]_{4-6}H$$

It is reported that simple heat curing results in the cleavage of phenyl groups, by the acidic protons of the Si—OH moieties, which leads to a network based on Si—O—Si crosslinks. This mechanism could account for the increased insolubility of the hydroxy-terminated (IX) over the trimethylsilyl-terminated (X) 10-SiB-4 ϕ polymers which occurred on heating.

The incorporation of a fraction of 10-SiB-4 ϕ into a 10-SiB-3 polymer is planned.[4] This could lead to a product that could be thermally cured

to about 475°C in nitrogen and which could contain crosslinks that would be expected to be thermally stable and evolve to better high-temperature elastomeric products.

SUMMARY AND CONCLUSIONS

This report on the physical and stability properties of the poly(carborane-siloxane)s listed in Table I has yielded much information about the nature of these materials.

Most of the polymers behave classically with respect to the glass transition and melting point. In the 10-SiB-x series, the glass transition temperatures behave according to the copolymer composition–glass transition relationship:

$$1/T_g = W(1)/T_g(1) + W(2)/T_g(2).$$

10-SiB-1 is an exception, and a theory of carborane cage association was proposed to explain this. Glass transitions were found to increase as the result of adding the bulky phenyl side groups, which decrease chain flexibility; as the result of replacing the kinked *meta*-carborane linkage with the colinear *para*-carborane linkage, which allows closer intermolecular packing; and as the result of adding bulky and polar trifluoropropyl side groups, which presumably increase both chain stiffness and intermolecular bonding. The fact that endgroups and molecular weight had no effect on the value of the glass transition temperature was as would be expected for "high" polymers.

The finding that a random versus a regular repeat unit had no effect on the value of the glass transition temperature of the amorphous 10-SiB-4 ϕ polymers indicates that their properties are determined primarily by intramolecular factors and not by intermolecular effects dependent on the relatively small phenyl groups (relative to the size of the repeat unit in VIII, IX, and X).[27] The relatively constant ratio T_m/T_g, for all the semicrystalline polymers except 10-SiB-1, points to a common relationship between structure and glass transition and between structure and melting point. The peculiarity of 10-SiB-1 may again be due to cage association. The effect of high molecular weight resulting in an amorphous rather than a semicrystalline polymer was akin to the behavior of paraffin waxes as the chain length is increased.

There was a secondary transition at $-135°C$ to $-140°C$ in all the totally methylated *meta*-carborane polymers (cf. $-115°C$ for the *para*-carborane sample), except 10-SiB-1, which had $T_{sec} = -90°C$. The underlying relaxation is not easily correlated to any particular submolecular motion which is common to all the repeat units. The temperature region of these relaxations is too high to be associated with motion of the methyl group.[28] It may be related to the —Si—O—Si— linkage or to the *meta*-carborane-to-silicon linkage. Similarly located peaks have been reported[12] for 5-SiB-x polymers incorporating a —CB$_5$H$_6$C— cage where the carbon atoms occupy equatorial meta positions. The $-180°C$ secondary transi-

tion for the trifluorpropyl-substituted 10-SiB-3 polymer correlates well with the low-temperature transitions in n-butyl and n-propyl methacrylate polymers, indicating that its origin most probably lies in the motion of the rather large trifluoropropyl group.

The thermal stability correlations for the polymers were not as clearcut as correlations of physical transitions, but certain trends were apparent. Differential thermal analysis of the polymers in inert atmosphere (argon or nitrogen) gave no indication of reactions occurring up to about 550°C. Thermogravimetric analysis indicated a linear increase in weight lost by 800°C with x in the 10-SiB-x series. This would minimize the probability of a cyclization mechanism for weight loss which has been well documented for poly(dimethylsiloxane).[22-24] As expected, the pure silicone lost all of its weight by 600°C. All the meta-carborane polymers except the fluorinated one had a major weight loss region near 550°C. The fluorinated polymer had lost 40% of its weight by 500°C. The end-groups appeared to have no effect within the 10-SiB-3 series. The higher molecular weight 10-SiB-3 polymer lost less weight than its lower molecular weight counterpart, perhaps because it contained a low proportion of low molecular weight volatiles; and the trifluoropropyl polymer lost about twice as much weight as did the methylated ones (it had twice the organic content) by 800°C. The para-carborane 10-SiB-3 appeared to be more stable than the corresponding meta-polymer, since the major weight loss region was 50°C higher, but it experienced the same total weight loss by 800°C as the meta-polymer, in apparent contradiction to a cyclization mechanism. In the 10-SiB-4 series, the phenylated polymers lost about one half the weight of the totally methylated polymer by 800°C.

Thermomechanical studies amplified the TGA data. Poly(dimethylsiloxane) did indeed not stiffen as it lost all of its weight. The lack of crosslinking was confirmed by solubility studies. The para-10-SiB-3 was interpreted to crosslink lightly near 400°C which was confirmed by a solubility study. The phenylated 10-SiB-4 polymers all experienced a sharp increase in rigidity at 430°C; 10-SiB-1 began to stiffen at 380°C. In the 10-SiB-x series, all but 10-SiB-1 did not stiffen until above 500°C, and meta-10-SiB-3 remained the most soluble after heating to 500°C. On this basis, and also from consideration of the thermomechanical behavior which resulted from heating the polymers to 625°C and from the observation that all the carborane polymers experienced a mode of stiffening near 560°C where meta-10-SiB-3 began a catastrophic stiffening, the methylated 10-SiB-3 was estimated to be the most stable. The high-temperature limit (in nitrogen at 3.6°C/min) for all the carborane polymers studied to date appears to be 560°C. In general, the materials which experienced less weight loss than 10-SiB-3 also experienced some mode of crosslinking or stiffening below 500°C (para-10-SiB-3, 10-SiB-1, and the three 10-SiB-4 polymers).

Studies on the oxidative stability of these materials are now in progress and future reports are planned.

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