

Thermomechanical Behavior of Poly(Carborane-Siloxane)s Containing $-\text{CB}_3\text{H}_5\text{C}-$ Cages

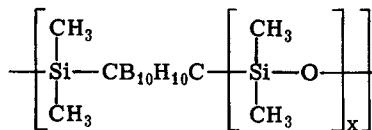
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Synopsis

The thermomechanical spectra of two new carborane-siloxane polymers containing five-boron carborane cages in the backbones are reported and discussed. The polymers are the homopolymer, $\text{HO}[\text{Si}(\text{CH}_3)_2\text{CB}_3\text{H}_5\text{C}\text{Si}(\text{CH}_3)_2\text{O}]_n\text{H}$, and the random copolymer with 20 mole-% of the ten-boron meta-carborane analogue, $[\text{Si}(\text{CH}_3)_2\text{CB}_{10}\text{H}_{10}\text{C}\text{Si}(\text{CH}_3)_2\text{O}]_x$. The mechanical spectra (~ 1 cps) were determined from $-180^\circ \rightarrow +625^\circ \rightarrow -180^\circ\text{C}$ ($\Delta T/\Delta t = 3.6^\circ\text{C}/\text{min}$ for $T > 25^\circ\text{C}$ and $2^\circ\text{C}/\text{min}$ for $T < 25^\circ\text{C}$) using the semimicro thermomechanical technique, torsional braid analysis. In nitrogen, both polymers displayed secondary transitions at -140°C . The glass transition (T_g) for the homopolymer was -60°C and for the copolymer was -52°C . The homopolymer had a melting point of $+70^\circ\text{C}$. The copolymer was amorphous. The high-temperature stability in nitrogen of both polymers appeared to be identical; thermal stiffening commenced at 400°C , continued to 625°C , and resulted in materials that were typical of highly crosslinked resins. In air, the homopolymer began to stiffen catastrophically near 270°C , while the copolymer began to stiffen similarly nearly 50°C higher. The intrinsic elastomeric nature together with the thermomechanical results prompted further study of the copolymer. Thermomechanical cycling studies in nitrogen and air are reported for the copolymer. Some correlating TGA and DTA are also discussed.

INTRODUCTION

Research in the field of high-temperature elastomers has led to the development and marketing of the carborane-siloxane polymers.¹⁻⁵ Most of the work to date has involved incorporation of the ten-boron meta-carborane cage (Fig. 1, top right) into a dimethylsiloxane backbone. The general structure of these polymers is structure I,



I

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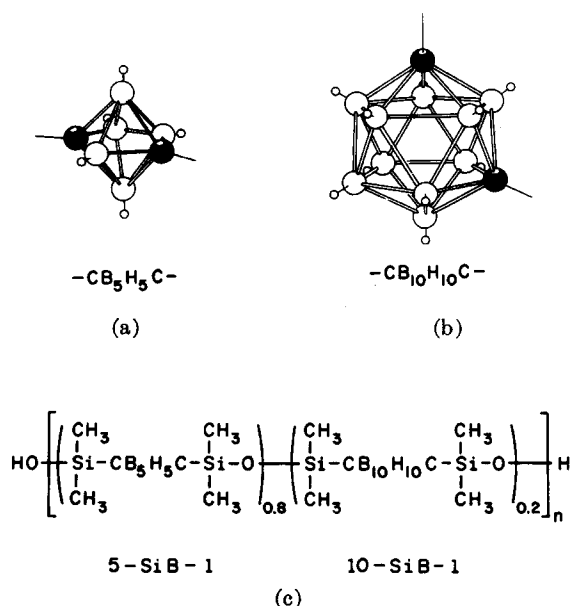
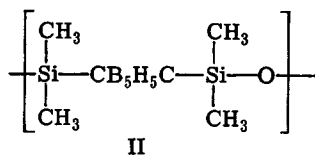


Fig. 1. Carborane-siloxane polymers: (a) B_5 carborane cage; (b) B_{10} carborane cage; (c) copolymer structure, 5-SiB-1 with 20% 10-SiB-1 in chain.

which has the designation 10-SiB-X, where 10 refers to the ten-boron cage and X to the number of oxygen atoms separating the cages in the polymer backbone. Carboranes with less than ten boron atoms per cage have been incorporated recently into linear poly(carborane-siloxane)s. The polymer with structure II,⁶



which is designated 5-SiB-1, contains a five-boron cage structure (Fig. 1, top left). Modified forms of 5-SiB-1 have been synthesized which contain a small fraction of larger carboranes (5–20% B_{10} and B_8),⁷ either in the backbone or in bulky side chains. These modifications were devised in an attempt to disrupt the crystallinity of 5-SiB-1 and render the polymer more elastomeric.

Studies of thermal and oxidative stability of the carborane-siloxane polymers have been of three types: (1) thermogravimetric and differential thermal analyses on uncompounded, compounded, uncured, and cured specimens^{7,8}; (2) ASTM tests, including hardness, tensile, compressive set, and elongation tests of cured and compounded specimens as functions of temperature and time^{2,3}; (3) chemical stress relaxation of cured, cross-linked, compounded, uncompounded, and crystalline specimens.^{9,10}

The present report deals with the application of the semimicro (i.e., <50 mg polymer) thermomechanical technique of torsional braid analysis (TBA)¹¹⁻¹³ in studying the thermomechanical properties of linear, uncompounded 5-SiB-1 homopolymer and a linear, random, uncompounded copolymer containing 20 mole-% 10-SiB-1. This copolymer was studied because of its inherent elastomeric character which was reported to be uncomplicated by crystallinity.⁷ The polymers (<1 g) were preliminary syntheses. The results bear on the inherent transitions and also on high-temperature stability of the linear polymers per se in nitrogen and in air. The report includes thermomechanical spectra (relative rigidity and mechanical damping versus temperature at ~ 1 cps) from -180° to $+625^\circ\text{C}$ and the results of thermomechanical cycling experiments which were designed to determine the effect of high-temperature history within this temperature range.

EXPERIMENTAL

Techniques

Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA). The TGA and DTA data were generated with a du Pont Model 900 instrument using heating rates of $3.6^\circ\text{C}/\text{min}$ (to correspond with the mechanical work) and $15^\circ\text{C}/\text{min}$, respectively, in both argon and air. The TGA specimens were prepared *in situ* by drying to 250°C in argon from 10% solutions (g polymer / ml chloroform).

Torsional Braid Analysis (TBA).¹¹⁻¹³ The thermomechanical data were determined throughout the range -180° to $+625^\circ\text{C}$ by the technique of torsional braid analysis which uses a modified torsional pendulum operating at about 1 cps. The torsional braid analyzer is a free-hanging torsional pendulum with the specimen consisting of a multifilamented (~ 3600) glass braid impregnated with the sample polymer. The specimen is fabricated *in situ* by removing solvent from a braid that has been soaked in a polymer solution before mounting. The specimens were dried to 250°C to remove solvent, stored overnight at 130°C in dried nitrogen, and taken through the temperature sequence of the experiment (130° to -180° to 625° to -180° to 25°C in nitrogen; 130 to 625 to 130°C in air). Attached to the lower specimen clamp is a polarizer disc, the inertial mass, which together with another polarizer, a light source, and a photocell acts also as a "linear with angle" optical transducer to convert the mechanical oscillations into electrical signals.¹³ The mechanical oscillations and the analogue signals approximate damped sine waves. The mechanical parameters are deduced from the character of the analogue signals. For isotropic, homogeneous specimens of sufficiently low damping, subject to small strains, $G' = K (1/P^2)$, where G' is the in-phase elastic modulus, P is the period of oscillation, and K is a constant dependent upon geometry; the logarithmic

decrement, a measure of the ratio of energy dissipated to maximum energy stored on mechanical deformation, is defined as

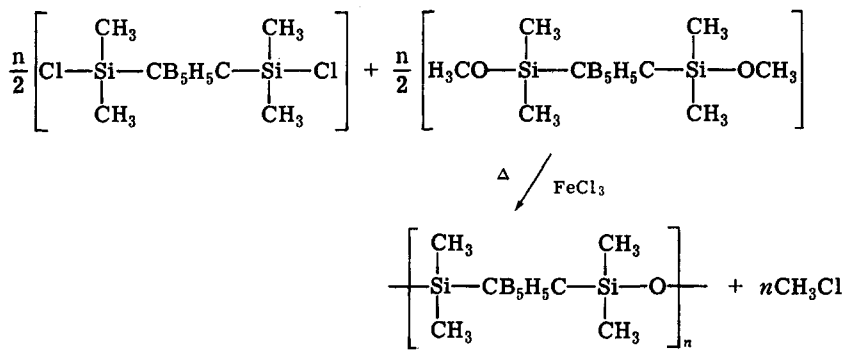
$$\Delta = \ln(A_1/A_2) = \ln(A_2/A_3) \dots = \ln(A_n/A_{n+1}).$$

Due to the composite nature, the small size, and the irregular geometry of the specimens, the work discussed herein is presented in terms of the relative rigidity, $(1/P^2)$, replacing G' . The logarithmic decrement (Δ) is presented as the mechanical damping index, $1/n$, where n is the number of oscillations between two fixed but arbitrary boundary amplitudes (e.g., $A_i/A_{i+n} = 20$, taken constant over any thermomechanical experiment); $1/n$ is directly proportional to the logarithmic decrement,

$$(\Delta = 1/n \ln[A_i/A_{i+n}]).$$

Materials

Structure and Synthesis.^{7,14} The homopolymer (II) was synthesized by Chemical Systems Incorporated, Santa Ana, California, by a dichloro-dimethoxy bulk condensation procedure using FeCl_3 as catalyst.^{7,14}



Equal moles of the two reactants with 2 mole-% anhydrous FeCl_3 as catalyst were heated to 185°C in an evacuated vessel. Additional FeCl_3 (2 mole-%) was added after 3 hr of reaction, and the reaction was continued until evolution of methyl chloride was complete. The polymer was isolated by dissolving the raw polymer in hot xylene, filtering, precipitating with methanol, washing with aqueous acetone, redissolving in xylene, and reprecipitating with methanol (yield 97.7%).^{7,14} This synthesis would be expected to produce a regular molecular structure, and the methyl proton NMR spectra substantiate this. The material was a hard, light-brown wax. The number-average molecular weight (M_n) was reported to be $12,500 \pm 10\%$ as determined by using solutions of the polymer in xylene in a Vapor Pressure Osmometer (Mechrolab Model 301A).¹⁴ A second sample, synthesized by a different mechanism at the Olin Research Center, New Haven, Connecticut, was also made available. This sample was prepared without FeCl_3 catalyst. The synthesis¹⁵ involved the bulk condensation of the dihydroxy monomer, $\text{B}_5\text{H}_5\text{C}_2\text{—}[\text{Si}(\text{CH}_3)_2\text{—OH}]_2$, at 150°—

180°C in the presence of tetramethylguanidine sulfate. The reaction product was dissolved in ether, extracted with water to remove catalyst residues, treated with aqueous NaHCO₃, washed, and filtered, and the solvent was removed in vacuo. This second sample had the appearance of candle wax. The average molecular weight was 18,000 as determined by the GPC peak. The methyl proton NMR and IR spectra indicate that the structure is the same as that of the light-brown homopolymer. The NMR and IR spectra of the two homopolymer samples are shown in the Appendix (Figs. 10 and 11).

The copolymer (5-SiB-1 with 20 mole-% 10-SiB-1 in the backbone, Fig. 1) was prepared, at Chemical Systems, Incorporated, by a procedure^{7,14} which was similar to the dichloro-dimethoxy homopolymer synthesis. The C₂B₁₀H₁₀ moiety was introduced to the reaction system in the methoxy form, CH₃O—Si(CH₃)₂—CB₁₀H₁₀C—Si(CH₃)₂—OCH₃. This synthesis would be expected to place the C₂B₅H₅ and C₂B₁₀H₁₀ cages randomly in the backbone (Fig. 1).¹⁶ The majority of the work on the copolymer used a sample with number-average weight, $M_n = 3830 \pm 10\%$. A sample with $M_n = 11400 \pm 10\%$ was received later from the same source, and some work on it is discussed. The lower M_n copolymer sample was received as a glossy, black, soft and elastic disc of low tensile strength and finite memory (e.g., finger prints remained after impression). The higher M_n sample was similar but harder than the former. The IR spectrum of the lower molecular weight copolymer is shown in the Appendix (Fig. 10).

RESULTS AND DISCUSSION

5-SiB-1 Homopolymer

Thermogravimetric Analysis and Differential Thermal Analysis. The TGA data indicated a high degree of thermogravimetric stability for the light-brown homopolymer (Fig. 2). In an inert environment (argon), weight loss commenced at 375°C, continued to 480°C (5% loss), then was linear to 700°C (8% loss) where it remained level to 800°C. In air, there was an initial weight gain of 1% to 280°C, where there was a loss of 2% (to 99% specimen weight); between 620°C and 800°C there was a weight loss of 2% (to a final weight of 97% of original specimen weight).

The DTA data (Fig. 2), in argon, on the "as received" light-brown homopolymer displayed an endothermic crystalline melting peak at 71°C. The remainder of the run was characterless to above 500°C. In air, the 71°C melting point (T_m) was evident, followed by a very shallow endotherm which led into a skewed exothermic peak beginning at 285°C—which corresponded to the weight gain detected via TGA—and peaked at 326°C. At 470°C, a very large exotherm began which corresponded to the onset of weight loss. The second sample of the homopolymer, synthesized by a different mechanism in a different laboratory, was also examined (see experimental section). The thermograms were virtually the same, the only difference being that the "white" polymer's exotherm peaked at 317°C

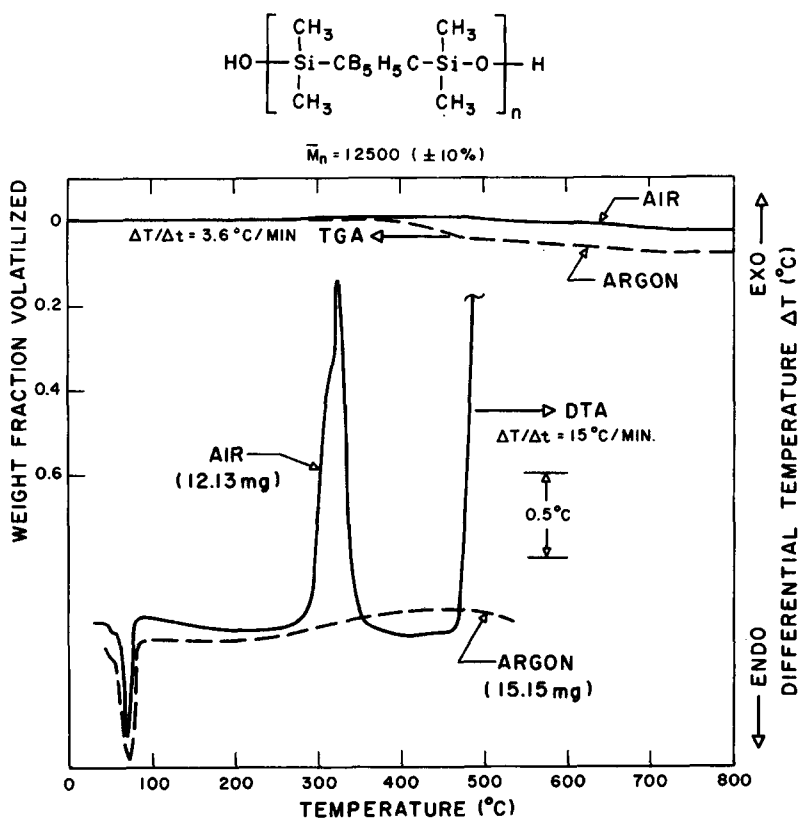


Fig. 2. TGA ($\Delta T/\Delta t = 3.6^\circ\text{C}/\text{min}$) and DTA ($\Delta T/\Delta t = 15^\circ\text{C}/\text{min}$) of 5-SiB-1 homopolymer, in argon and air.

rather than at 326°C , which indicated little difference between the polymers. The oxidative results agree with previously published data on the homopolymer.¹⁴

Thermomechanical Behavior. The thermomechanical behavior of the 5-SiB-1 polymers at about 1 cps in flowing dried nitrogen and in flowing air were obtained on specimens which were prepared by heating in situ (at $2^\circ\text{C}/\text{min}$ to 250°C under flowing dried nitrogen) a glass braid soaked in a 10% (g polymer/ml chloroform) solution. The specimens were stored overnight in the apparatus at 130°C under nitrogen. The temperature sequences of the experiments were 130° to -180° to 625° to -180°C to 25°C in nitrogen, and 130° to 625° to 130°C in air.

Thermomechanical spectra in dried nitrogen are shown in Figure 3. On cooling from 130°C , crystallization was accompanied by a damping maximum at 50°C (0.3 cps), the glass transition (T_g) occurred at -60°C (0.7 cps), and a low-temperature transition (T_{sec}) was revealed at -140°C (0.9 cps). On subsequent heating from -180°C , some thermohysteresis was displayed which, for the most part, occurred above T_g (the consequence

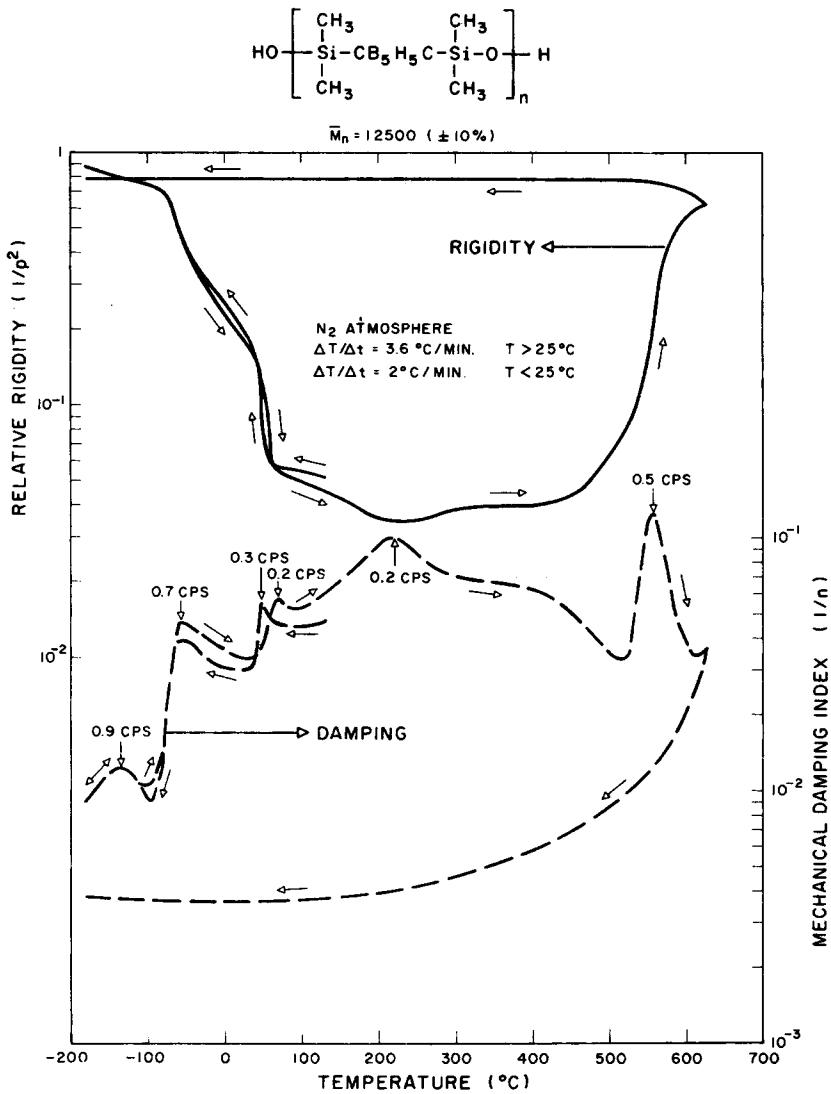


Fig. 3. Thermomechanical spectra of 5-SiB-1 homopolymer in nitrogen ($\Delta T/\Delta t = 3.6^\circ\text{C}/\text{min}$, $T > 25^\circ\text{C}$; $\Delta T/\Delta t \approx 2^\circ\text{C}/\text{min}$, $T < 25^\circ\text{C}$), from $130^\circ \rightarrow -180^\circ \rightarrow 625^\circ \rightarrow -180^\circ \rightarrow 25^\circ\text{C}$.

of the crystallinity); T_m was 70°C (0.2 cps). Above 150°C , the rigidity dropped to a minimum near 200°C and then rose to a plateau at about 320°C . The damping had a corresponding peak at 220°C . The rigidity rose sigmoidally from 400°C to 625°C , presumably because of crosslinking. This corresponded to the weight loss region indicated by the TGA data in argon. The largest increase in rigidity occurred above 480°C , where the rate of weight loss decreased drastically. It is reasonable to expect that

once a linear structure has begun to crosslink, the rate of weight loss accompanying further degradation could decrease. The damping peak at 560°C corresponded to the catastrophic increase in rigidity. On cooling from 625°C to -180°C, the rigidity rose to a high constant level by 500°C, and the damping dropped to a very low level. These latter features are characteristic of a highly crosslinked resin. (After the pyrolysis, the curves below 25°C were reversible.)

The second sample of the 5-SiB-1 polymer (discussed above, prepared with tetramethylguanidine sulfate as catalyst) displayed T_g , T_m , and low-temperature transitions identical (not shown) to those of the apparently less pure, light-brown first sample.

Thermomechanical behavior in air of a further specimen of the first (light-brown) homopolymer is shown in Figure 4. The rigidity decreased slightly from 130°C to 250°C, after which it rose sharply to a broad maximum in the vicinity of 380°C to 400°C. The latter corresponds to the increase in weight detected by TGA and the large exotherm observed by DTA (Fig. 2). There was a minimum in rigidity at 460°C and then a large sigmoidal rise, corresponding to the weight loss region, which flattened out in the 600°-625°C range. The damping rose slowly from 130°C to a sharp peak at 295°C, which corresponded to the first rise in rigidity. There was a damping minimum at 375°C which led to a broad flat peak in the 450°-530°C range. On cooling from 625°C, the rigidity increased slowly to a constant high level below 400°C. Correspondingly, the damping decreased below 625°C to a minimum at 580°C, increased to a peak at 465°-470°C, after which it dropped sharply to a very low level below 300°C. The behavior of the rigidity and damping indicates the presence of a broad T_g region between 400°C and 500°C for the homopolymer after oxidative cure to 625°C (at 3.6°C/min).

The second homopolymer sample, described above, was also examined oxidatively. The thermomechanical spectra in air (not shown) of this "white" homopolymer were identical to those of the previously discussed light-brown wax, with the one exception that the first rise in rigidity (above 250°C) was smaller. This was probably due to differences in melt elasticity which were related to differences in molecular weight and molecular weight distribution.

5-SiB-1 Copolymer

Thermogravimetric Analysis and Differential Thermal Analysis. The copolymer TGA and DTA specimens were prepared and run in the same manner as were those of the homopolymer. The TGA and DTA data are shown in Figure 5.

The TGA data both in argon and in air for the copolymer were similar to those of the homopolymer, with the following exceptions. First, in argon the onset of weight loss was at 250°C (cf. 375°C for the homopolymer), although the major mode of weight loss appeared to commence at 375°C. Correspondingly, in air the same initial weight loss occurred as in

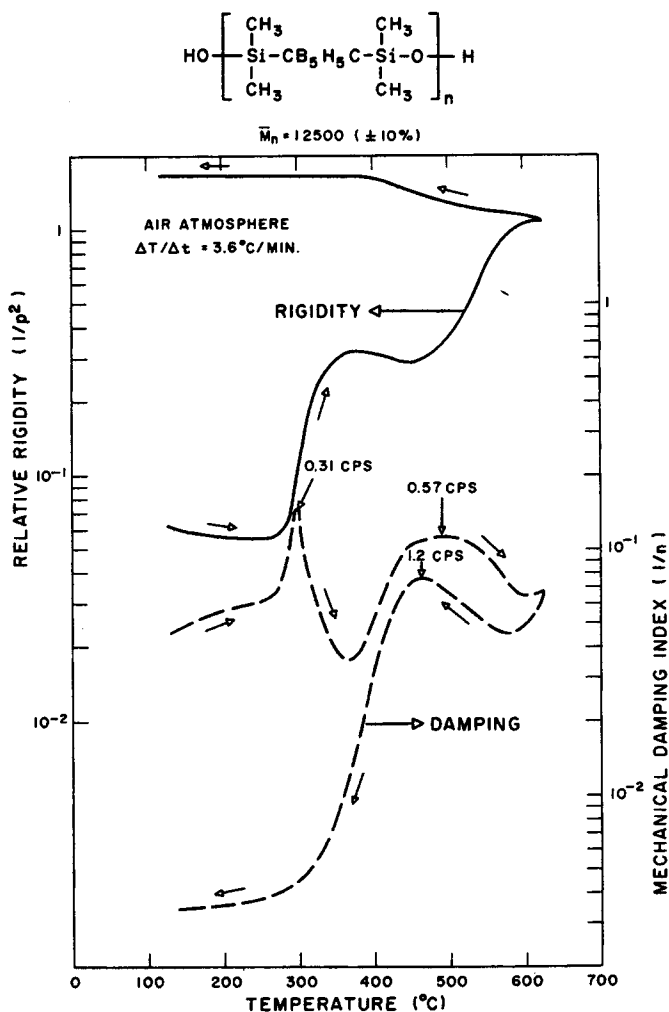


Fig. 4. Thermomechanical spectra of 5-SiB-1 homopolymer in air ($\Delta T/\Delta t = 3.6^\circ\text{C}/\text{min}$), from $130^\circ \rightarrow 625^\circ \rightarrow 130^\circ\text{C}$.

argon (2%), and then a weight gain occurred at 350°C (cf. 280°C for the homopolymer). The initial loss of weight may have been due to the larger amount of low molecular weight material in the copolymer ($M_n = 3830$) relative to the homopolymer ($M_n = 12,500$). The weight loss by 800°C in argon was 13% (versus 8% for the homopolymer) and was 0% in air (versus 3% for the homopolymer).

The DTA data in argon on the "as received" copolymer revealed a very small but sharp endothermic peak (T_m) at about 51°C (cf. $T_m = 70^\circ\text{C}$ for the homopolymer) and displayed behavior similar to that of the homopolymer above 100°C . The sample was insoluble after the DTA run to 530°C and appeared to have retained its original shape. Another specimen

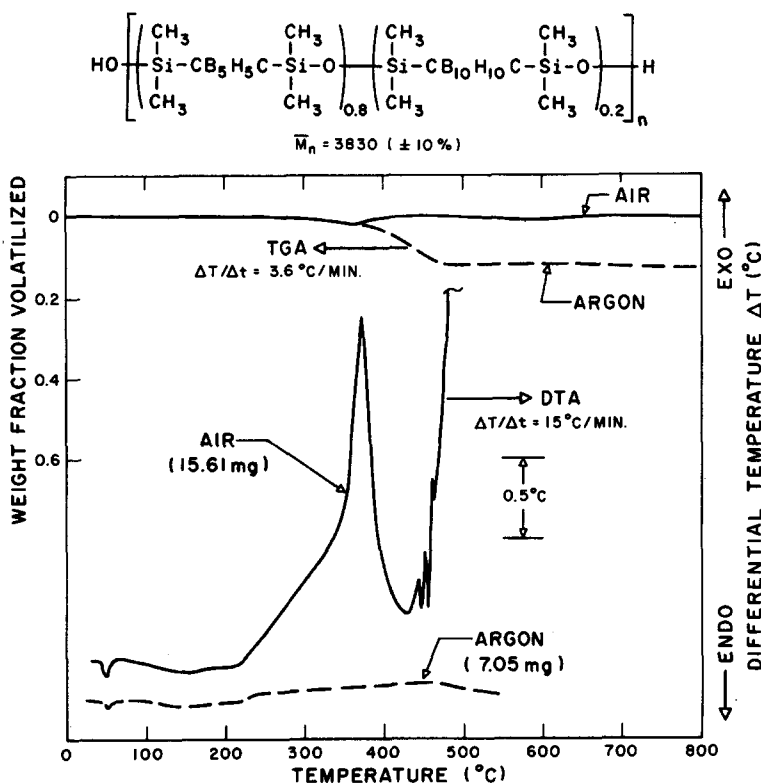


Fig. 5. TGA ($\Delta T/\Delta t = 3.6^\circ\text{C}/\text{min}$) and DTA ($\Delta T/\Delta t = 15^\circ\text{C}/\text{min}$) of 5-SiB-1 with 20% 10-SiB-1 in chain, in argon and air.

remained soluble after heating to 350°C at $3.6^\circ\text{C}/\text{min}$ in nitrogen, indicating that the crosslinking occurred above 350°C . In air, the DTA plot was identical to that in argon until 230°C , where a steady exothermic shift began, indicating a lower temperature for the onset of oxidative reaction relative to the homopolymer; above 350°C , the shift accelerated and peaked at 373°C . (The corresponding peak temperature was 326°C for the homopolymer.) At about 470°C , another large exotherm began, as had been seen for the homopolymer. DTA data for both samples of the copolymer ("as received") were similar, with the exception of the intensity of the 51°C endotherm which was five times as large (area/mg) for the sample with higher M_n . Another low M_n specimen of the "as received" polymer was preheated at $3.6^\circ\text{C}/\text{min}$ in nitrogen to 250°C and cooled to room temperature before being placed, several days later, in the DTA sample holder; it was then run in air as previously described. The only apparent difference was the disappearance of the small 51°C endotherm for the preheated specimen. This indicated that a small degree of crystallization occurred on prolonged standing, as had been reported for similar copolymers incorporating less $\text{C}_2\text{B}_{10}\text{H}_{10}$.¹⁴ The crystallinity appeared to be eliminated in the initial

heating cycle. The value of 51°C for T_m compares favorably to the values of 57°, 56°, and 52°C previously reported¹⁴ by differential scanning calorimetry (DSC) for copolymers with 5%, 10%, and 15% (mole-%) $C_2B_{10}H_{10}$ in the polymer chain. The different degrees of crystallinity for the $M_n = 3830$ and $M_n = 11400$ samples would contribute to the different appearances and "feel" of the two "as received" samples. Heating a specimen of the $M_n = 11400$ sample to 250°C (3.6°C/min) in argon made it feel more like the softer, lower molecular weight sample at room temperature.

The TGA and DTA data alone, for the homopolymer and copolymer, would suggest, to some, a rather high degree of thermal stability to 500°C and above. Oxidatively there was a high degree of stability in terms of weight loss, but the large exotherm in air (DTA) and the TGA results in argon suggest that the lower weight loss in air was related to a reaction occurring in the neighborhood of 300°–350°C.

Thermomechanical Behavior. The specimens for TBA were prepared from a 10% solution in xylene for the $M_n = 3830$ sample and from a 10% solution in chloroform for the $M_n = 11400$ sample, in the manner described above for the homopolymer. The solutions of both copolymer samples contained some fine black particles which settled out on standing.

The thermomechanical spectra, in dried nitrogen, of the copolymer are displayed in Figure 6. There was a damping peak at -52°C (0.65 cps), accompanied by a large decrease in rigidity. This corresponds well to the value of -54°C for T_g determined by DSC.¹⁴ The glass transitions of -60°C and -52°C for the homopolymer and copolymer, respectively, are indicative of a high degree of flexibility in the polymer chain and of a high free volume which could result from the kinked nature of the molecular chain. It is interesting to compare the behavior with that of the analogous 10-SiB-X polymers for which data on the transitions as a function of X are available.¹⁷ The 5-SiB-1 polymer ($T_g = -60°C$) corresponds most closely to the 10-SiB-3 polymer ($T_g = -68°C$) which has four more flexible silicon-oxygen bonds in the repeat unit. This leads to the conclusion that the carborane cage influences the transitions and/or the carbon-silicon bond differs significantly in its nature and flexibility depending on the type of carborane cage in which the carbon is incorporated.

Application of the empirical copolymer relationship¹⁸

$$1/T_g = W_1/T_{g1} + W_2/T_{g2}$$

to the above glass transition temperatures for the homopolymer and copolymer, where W_1 and W_2 are the weight fractions of each of the two components of the copolymer, predicts a T_g for 10-SiB-1 of -24°C. Although this does not correspond to the reported value of +25°C,^{9,17} it does indicate a significantly higher intrinsic stiffness for 10-SiB-1 relative to 5-SiB-1. (In general, 10-SiB-1 has been found to display a peculiar set of physical properties within the 10-SiB-X series.¹⁷) Extending this approach to the homopolymer (i.e., 5-SiB-1 as a 1:1 copolymer of 5-SiB-O and di-

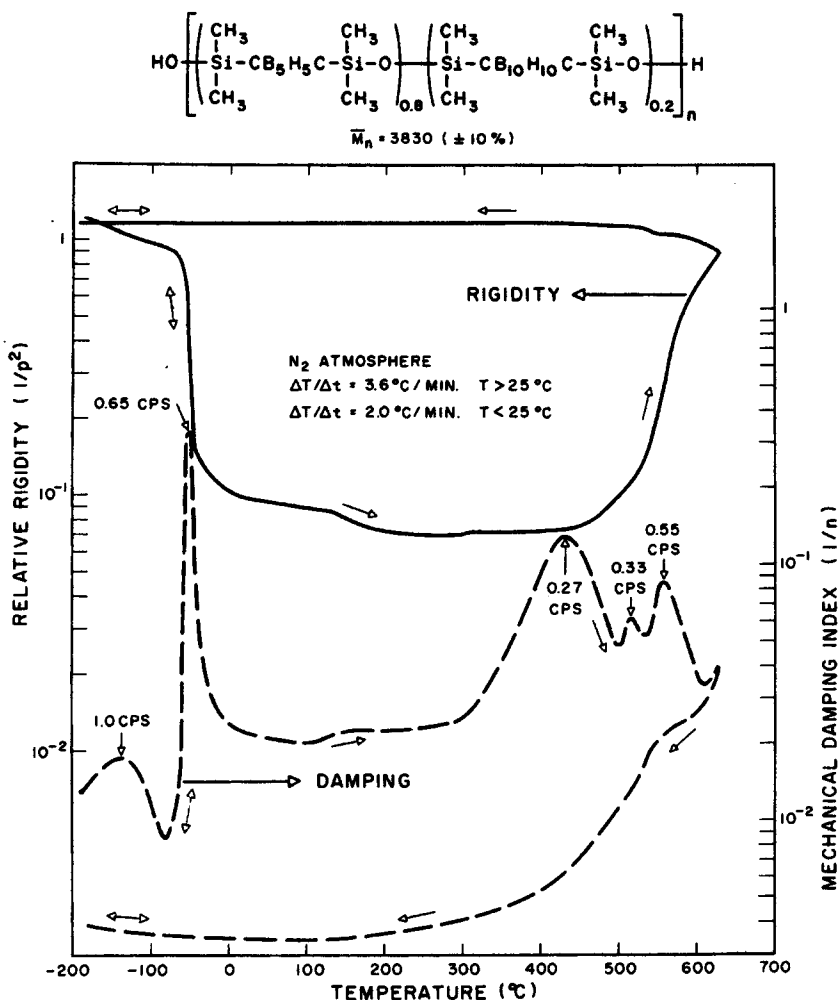


Fig. 6. Thermomechanical spectra in nitrogen ($\Delta T/\Delta t = 3.6^\circ\text{C}/\text{min}$, $T > 25^\circ\text{C}$; $\Delta T/\Delta t \approx 2.0^\circ\text{C}/\text{min}$, $T < 25^\circ\text{C}$), of 5-SiB-1 with 20% 10-SiB-1 in chain, from $130^\circ \rightarrow -180^\circ \rightarrow 625^\circ \rightarrow -180^\circ \rightarrow 25^\circ\text{C}$.

methylsiloxane repeat units) and assuming that the equation would apply to the nonrandom copolymer, the equation predicts a T_g for $-\text{Si}(\text{CH}_3)_2-\text{CB}_5\text{H}_5\text{C}-$ of $+3^\circ\text{C}$. If valid, this would again demonstrate the unusual flexibility of the particular silicon-carbon (carborane) bond. The non-applicability of the equation to this alternating copolymer would be attributable to the effect of regular in-chain geometry on intermolecular interaction and not on inherent chain flexibility.^{17,19}

In the glassy state, there was a small, well-defined damping peak at -140°C (1.0 cps) which was accompanied by an inflection in the rigidity curve (data were reversible on cooling and reheating). A similarly located

secondary transition was revealed in the glassy state of the 5-SiB-1 homopolymer (Fig. 3) and has been reported for most of the 10-SiB-X metacborane polymers studied to date.¹⁷ (The 10-SiB-1 polymer has a T_{sec} at -90°C .)¹⁷ In the range of 130°C to 160°C , there was a small drop in modulus and increase in damping similar to that noted in the homopolymer. At about 295°C , a small step-rise in rigidity occurred which was accompanied by the onset of a large damping peak which reached a maximum at $\sim 425^{\circ}\text{C}$ (0.27 cps). The rigidity began to rise further at 400°C . There was a very small damping peak at 515°C (0.33 cps) and another larger one at 560°C (0.55 cps). The high temperature responses ($T > 400^{\circ}\text{C}$) in nitrogen of the homopolymer and the copolymer were virtually identical, with the rigidity rising sigmoidally from 400°C to 625°C . On cooling from 625°C , the rigidity experienced a small step-rise at about 550°C (this temperature is sensitive to the time lapsed reversing the direction of temperature programming) and was accompanied by a shoulder in the rapidly decreasing damping. The rigidity remained flat from 550°C to -180°C (and back reversibly to 25°C). The damping, below 300°C , remained at a low, almost constant level (also reversible from below 25°C).

A specimen made with the copolymer sample of $M_n = 11400$, examined in a similar manner, gave identical results (not shown), with a few minor exceptions: (a) the step-rise in rigidity at 290°C was not present; (b) the 515°C damping peak was not present; and (c) the 560°C damping intensity was about the same as the 425°C peak (unlike that for the $M_n = 3830$ sample, where it was smaller). It is interesting to note that the T_g (-52°C) and the secondary transition T_{sec} (-140°C) were not shifted when the number-average molecular weight of the polymer was changed from 3830 to 11400. The sample of the lower M_n "as received" polymer that was preheated at $3.6^{\circ}\text{C}/\text{min}$ in argon to 250°C before the oxidation DTA run (see above) showed evidence of puckering and bubble marks, indicating that some low molecular weight volatiles had been driven off, whereas a specimen of the $M_n = 11400$ sample did not display evidence of bubbling. (These volatiles may contribute significantly to the low M_n reported for the first sample.) The thermal prehistory of the TBA specimens would have driven off any low molecular weight volatiles—in effect increasing M_n .

In air, the rigidity increased slowly above 175°C until 340°C , where it rose sharply to a maximum between 420°C and 445°C . There was a small drop in rigidity at 460°C and then a slow rise to about the same level as the maximum reached at 420°C . These features were less pronounced than for the homopolymer. The damping started with a small increase (as in nitrogen), but at 200°C it began a large rise to a shoulder between 290°C and 320°C . There was a sharp peak at 360°C , a minimum at 400°C , and a broad peak near 520°C which decreased to 625°C . The maximum in the rigidity curve could indicate that there was a scission reaction near 450°C competing successfully with the stiffening reaction, or that the new material formed during the stiffening process (340°C to 420°C)

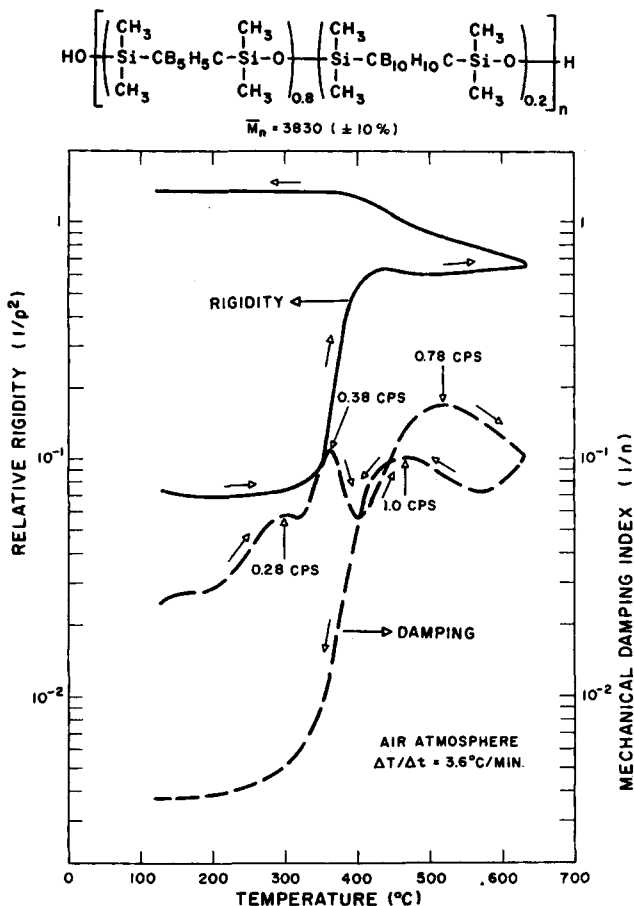


Fig. 7. Thermomechanical spectra in air ($\Delta T/\Delta t = 3.6^\circ\text{C}/\text{min}$), of 5-SiB-1 with 20% 10-SiB-1 chain, from $130^\circ \rightarrow 625^\circ \rightarrow 130^\circ\text{C}$.

was experiencing a physical transition (e.g., T_g). The thermal (in argon) TGA curve displayed the maximum rate of weight loss in this region for the linear copolymer. This led to the conclusion that the reduction in rigidity observed during oxidation, in the already highly crosslinked network, had the same thermal origin as the weight loss experienced in the absence of air while the chains are still mobile (i.e., scission). A similar argument holds for the maximum in the rigidity noted for the homopolymer. On cooling from 625°C , the rigidity increased slowly through what appeared to be a broad glass transition region between 400° and 500°C ; from 400° to 120°C , the rigidity was flat. Correspondingly, the damping decreased from 625°C to 570°C ; there was a broad peak at 460°C and a large decrease between 410 and 300°C , below which the decrease continued slowly. The mechanical behavior of the copolymer oxidatively cured to 625°C and the similarly treated homopolymer were almost identical.

Comparison of the oxidative thermomechanical data for the homopolymer and the copolymer indicated that, although the homopolymer's crosslinking threshold temperature ($\Delta T/\Delta t = 3.6^\circ\text{C}/\text{min}$) was 50°C lower than that of the copolymer (which is about 340°C), the initial stage (to about 400°C) of crosslinking in the homopolymer resulted in a less densely crosslinked structure. This is evidenced for the homopolymer; first, by the lower rigidity at 400°C (relative to the final crosslinked product); second, by the larger subsequent decrease in rigidity by 460°C , which is apparently due to thermal scission of a looser network; and third, by a large degree of subsequent stiffening which corresponds to the formation of a very tightly crosslinked system—possibly of similar origin to the catastrophic stiffening observed in nitrogen in the same temperature range ($450^\circ\text{--}625^\circ\text{C}$).

Thermomechanical cycling experiments were carried out on the $M_n = 3830$ copolymer in both nitrogen and air (Figs. 8 and 9). The cycles were closed loops from 130° to -180°C to cycle maximum temperature to 130°C , with the final segment from 130° to -180° to 20°C (to test for reversibility of the low-temperature region after pyrolysis). In nitrogen, the maximum cycle temperatures were 350° , 450° and 550°C . In air, they were 250° , 350° and 450°C . In general, the cycling data amplify the data of the continuous spectra (i. e., Figs. 6 and 7).

The first new information is that the 130° to 160°C damping shoulder and the drop in rigidity (Fig. 6) were not reversible on heating and subsequent cooling. This was observed in both nitrogen (to 350°C) and air (to 250°C) cycling. The lack of change in the properties of the inert glass substrate per se at 130°C coupled with the response of the glass/polymer composite (Figs. 8 and 9) points to some change in the properties of the polymer or in a composite property in this temperature range. It is noteworthy that the heating portion of the thermohysteresis loop of the first cycle was reproduced in the heating portion of the second cycle of the experiments.

The next interesting feature of the cycling experiments is that in both cases the first cycle (to 350°C in nitrogen and to 250°C in air) had no apparent effect on the secondary transition (-140°C) or on the glass transition temperature (-52°C). This was in spite of the fact that, in both cases, the damping had begun to rise (before the maximum temperature of the cycle was reached) toward the peaks seen in the continuous spectra. In the air run, the cycle was within the region of significant exothermal shift (DTA). In other experiments, it was found that the applied heating cycle (to 350°C in nitrogen and to 260°C in air) left the polymer soluble in xylene, indicating that no significant crosslinking had occurred.

In the second cycle of each experiment (to 450°C in nitrogen; to 350°C in air) the polymer entered a reaction region. In both cases the rigidity was higher on cooling from the cycle maximum than before heating up to it. The increase in rigidity in the air run was significantly higher than in the nitrogen run. This was consistent with the relative shapes of the continuous spectra (Figs. 6 and 7) in the temperature region of the maximum

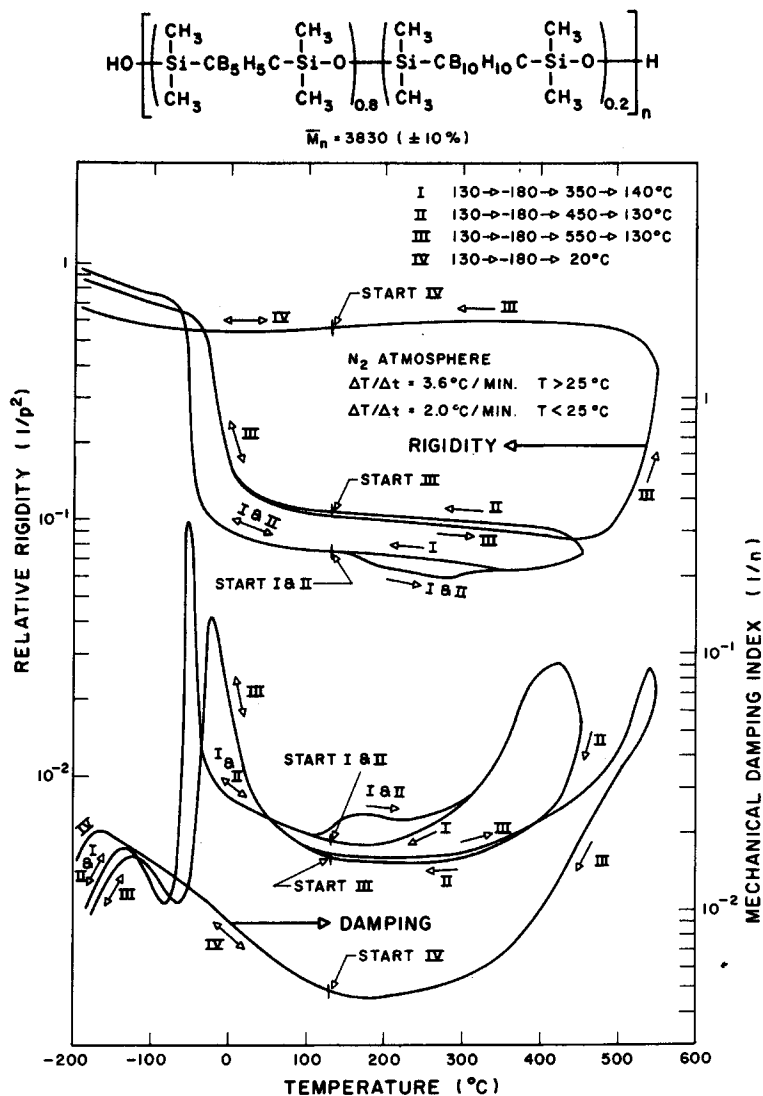


Fig. 8. Thermomechanical cycling ($\Delta T/\Delta t = 3.6^\circ\text{C}/\text{min}$, $T > 25^\circ\text{C}$; $\Delta T/\Delta t \approx 2^\circ\text{C}/\text{min}$, $T < 25^\circ\text{C}$) of 5-SiB-1 with 20% 10-SiB-1 in chain, in nitrogen: (I) $130^\circ \rightarrow -180^\circ \rightarrow 350^\circ \rightarrow 140^\circ\text{C}$; (II) $130^\circ \rightarrow -180^\circ \rightarrow 450^\circ \rightarrow 130^\circ\text{C}$; (III) $130^\circ \rightarrow -180^\circ \rightarrow 550^\circ \rightarrow 130^\circ\text{C}$; (IV) $130^\circ \rightarrow -180^\circ \rightarrow 20^\circ\text{C}$.

temperature of each cycle. The damping level in both cases decreased, and the glass transition peak broadened, decreased in intensity, and was shifted up to about -25°C . In nitrogen, the -140°C damping peak shifted to -130°C , and its intensity decreased slightly. In air, the -140°C peak was not shifted in temperature but decreased in magnitude significantly. The effect of each environment on the glassy-state secondary transition most probably resulted from a different type of restriction

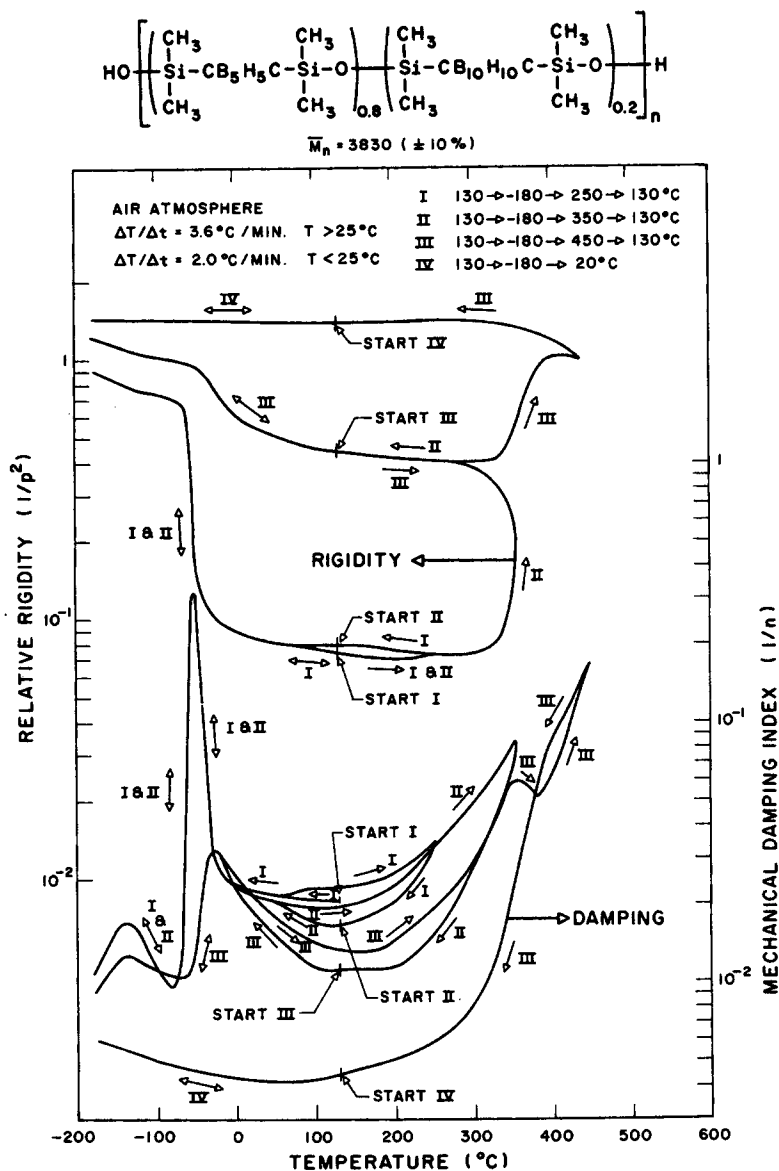


Fig. 9. Thermomechanical cycling ($\Delta T/\Delta t = 3.6^\circ\text{C}/\text{min}$, $T > 25^\circ\text{C}$; $\Delta T/\Delta t \approx 2^\circ\text{C}/\text{min}$, $T < 25^\circ\text{C}$) of 5-SiB-1 with 20% 10-SiB-1 in chain, in air: (I) $130^\circ \rightarrow -180^\circ \rightarrow 250^\circ \rightarrow 130^\circ$; (II) $130^\circ \rightarrow -180^\circ \rightarrow 350^\circ \rightarrow 130^\circ$; (III) $130^\circ \rightarrow -180^\circ \rightarrow 450^\circ \rightarrow 130^\circ$; (IV) $130^\circ \rightarrow -180^\circ \rightarrow 20^\circ\text{C}$.

on the submolecular motion which is related to that transition and leads to the conclusion that the crosslinking sites for the two environments were different.

In the third cycle of each experiment (550°C in nitrogen, 450°C in air), the material progressively entered the mechanical state of highly cross-

linked rubber and highly crosslinked resin, respectively. The nitrogen pyrolysis (to 550°C) product was a highly crosslinked rubber since it displayed a small *decrease* in rigidity with *decreasing* temperature below 330°C (i.e., G' has a positive temperature coefficient) and an increase on further cooling. This is typical elastomeric behavior and has been observed with several other carborane-siloxane polymers studied in this laboratory.¹⁷ The master curve (Fig. 6) in nitrogen showed that the polymer was a highly crosslinked resin after being heated to 625°C.

The low-temperature damping peak (-140°C in both polymers) revealed the onset of some submolecular motion more localized than that associated with T_g . The absence of low-temperature damping peaks after pyrolysis to 625°C and also after oxidation to 450°C indicated that the crosslinking occurred at a short enough range to prevent the localized motion related to the -140°C transition of the linear polymer. Thermal and oxidative cycling data show the effect of increasing crosslink density on both T_g and the secondary transition. A difference between the nitrogen and air cycling experiments was that, in nitrogen, each successive cycle decreased the rigidity in the glassy state (until the 625°C turnaround of the continuous spectra brought the rigidity of the crosslinked resin above that of the uncrosslinked glass), whereas the glassy state rigidity of the oxidative curve increased with each cycle. Although weight loss can affect relative rigidity in the manner seen in nitrogen on account of changes in geometry,¹³ a study of the TGA data showed that the large change in weight occurred in the temperature range where the decrease in rigidity was small, and vice versa. Correspondingly, after thermal cure in nitrogen, all the TBA specimens were stiff, glassy rods that were easily manipulated at room temperature, while those which were removed after oxidation were brittle to the point that not one was removed from the apparatus without breaking.

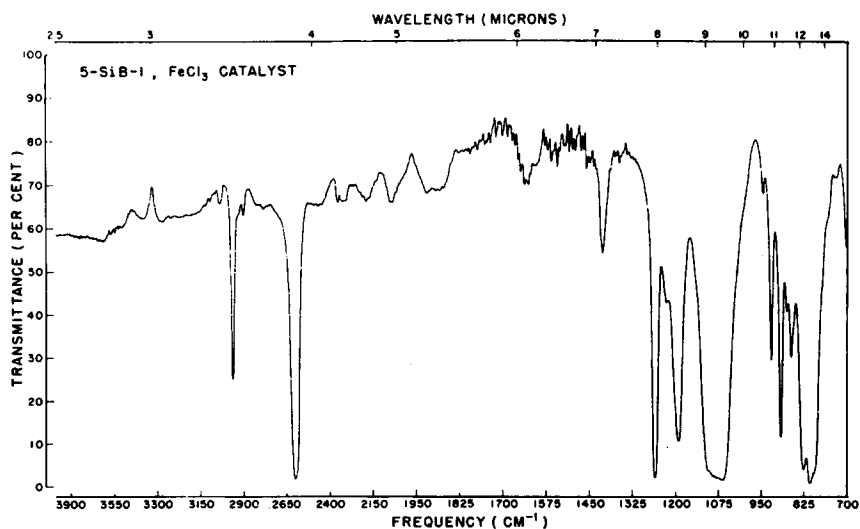
CONCLUSIONS

Thermomechanical spectra (at 3.6°C/min) in nitrogen of linear 5-SiB-1 polymer, and of a linear copolymer of 5-SiB-1 with 20 mole-% 10-SiB-1 in the backbone, indicated that the polymers do not begin to crosslink until above 400°C. In air, the copolymer appeared to be quite stable to about 300°C, where crosslinking occurred. The homopolymer appeared to be less stable oxidatively, and crosslinking commenced at about 250°C. (This difference may have been due in part to ferric ion impurities in the black copolymer acting as oxidative stabilizers.)

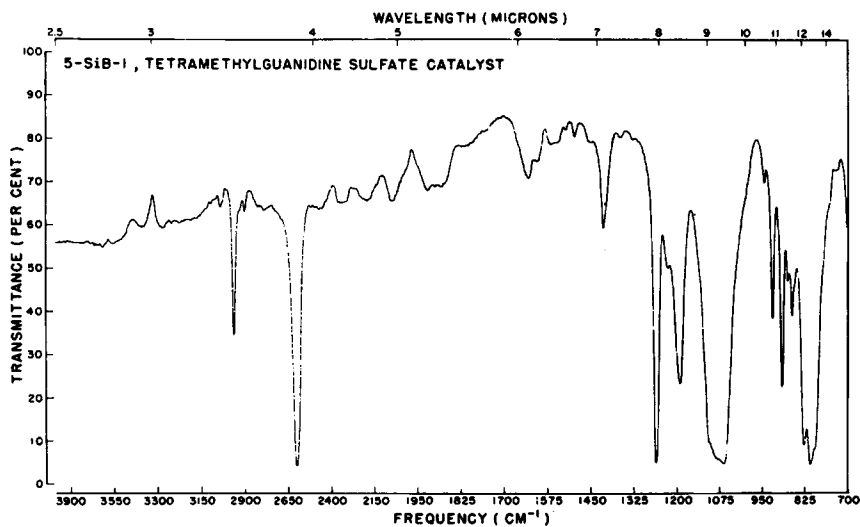
The mechanical data on the polymers indicated that the low level of weight loss in air and in argon revealed by TGA was due to the formation of crosslinks (cf. poly(dimethylsiloxane) decomposition, which in an inert atmosphere gives cyclic volatiles). The DTA data in argon gave no hint of the crosslinking that occurred below 500°C, whereas DTA data in air did correspond well to the rapid stiffening detected by TBA. This points out the problem of trying to evaluate, via TGA and DTA, a material whose

proposed applicability (e.g., an elastomer) is very sensitive to its structure (e.g., degree of crosslinking). On the other hand, comparison of the oxidative DTA and TBA data indicate different relative onset temperatures of oxidative attack for the homopolymer versus the copolymer. It is evident that a multitechnique approach must be used in order to establish criteria of stability.

From the TBA data at 3.6°C/min, the following broad categories have been established to reflect the state of the 5-SiB-1-20% 10-SiB-1 copolymer:

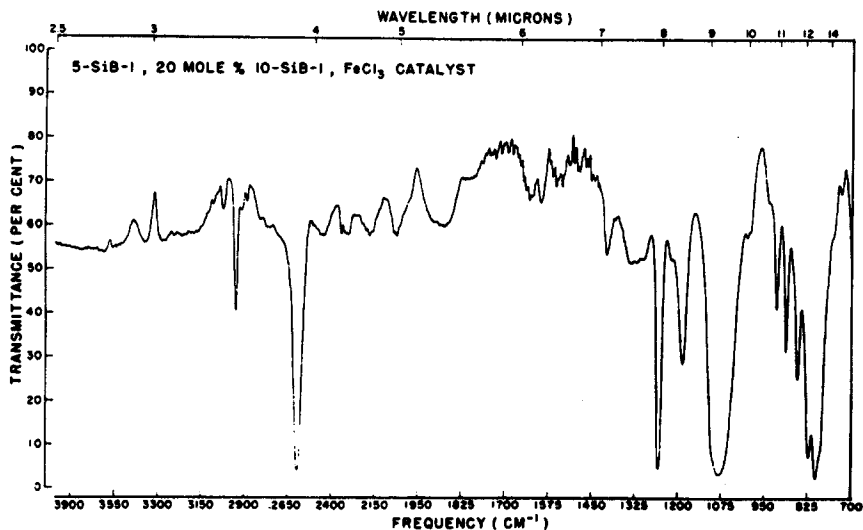


(a)



(b)

Fig. 10. (continued)



(c)

Fig. 10. Infrared spectra of the 5-SiB-1 homopolymers (a and b) and copolymer (c).

in nitrogen, a linear polymer to 400°C, a rubber to 500°C and a thermoset resin to 625°C; in air, a linear polymer to 300°C, a rubber to 350°C, and a thermoset resin to 625°C. The states of the homopolymer in nitrogen were similar, with the low-temperature properties reflecting the crystallinity, different glass transition temperature, and similarly located secondary transition of the material. The homopolymer in air was a linear polymer to about 250°C, a hard rubber to 450°C, and a thermoset to 625°C.

From the point of view of designing an elastomer with stability at elevated temperatures, the advantage gained by adding 20% $\text{—CB}_{10}\text{H}_{10}\text{C—}$ to the 5-SiB-1 backbone is indicated by the virtually identical high-temperature mechanical properties of the two polymers in nitrogen and the improved mechanical properties of the copolymer relative to the homopolymer in air, while the useful low-temperature limit, as an elastomer, is extended from the 70°C T_m of the homopolymer to the -52°C T_g of the copolymer.

Appendix

The infrared spectra of the two samples of the 5-SiB-1 homopolymer ("light-brown" made with FeCl_3 catalyst, and "white" made with tetramethylguanidine sulfate catalyst) and the lower molecular weight ($\bar{M}_n = 3830$) copolymer sample are shown in Figure 10. The specimens were films cast from chloroform solution on NaCl plates and dried at about 35°C under vacuum (<2 mm Hg). The spectra were generated on a Beckman IR-12 instrument. The two homopolymer spectra are identical. The spectrum of the copolymer differs from that of the homopolymer mainly in the broad absorption band in the 1325 cm^{-1} region.

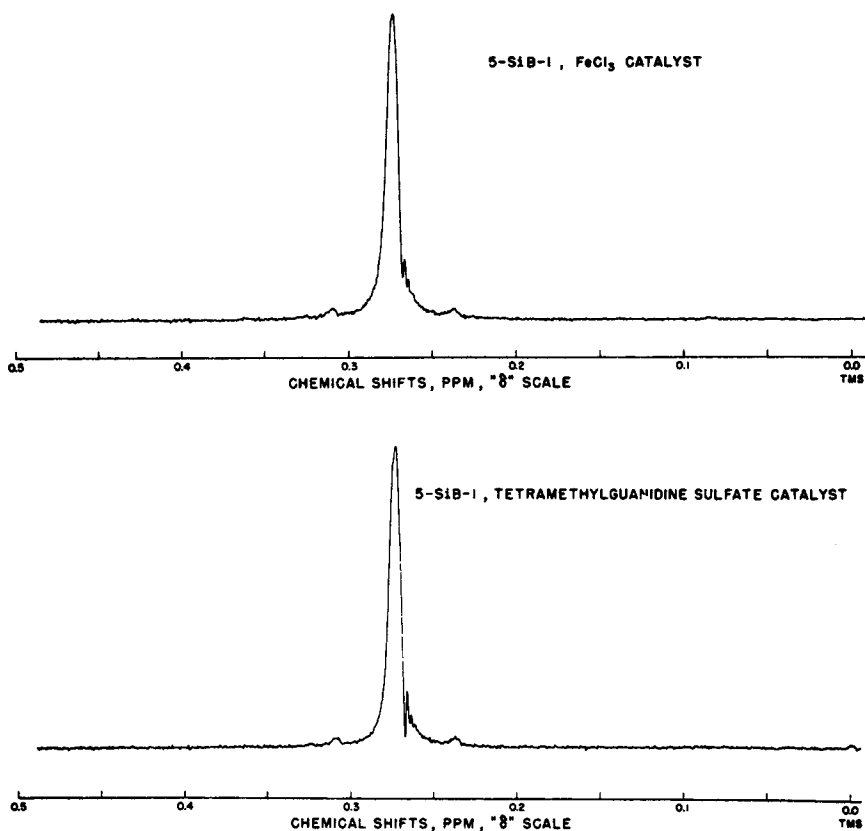


Fig. 11. High-resolution 100-MHz NMR spectra obtained at 25°C using 5% solutions of polymer in CDCl_3 .

The methyl proton NMR spectra of the two homopolymer samples are shown in Figure 11. The spectrum of the copolymer was not determined since fine particles which settled out on formation of the solution interfered with the determination of the spectra. It is felt that these particles were related to the FeCl_3 catalyst and that it was the iron present that interfered with the generation of the spectra. The spectra were generated on a Varian HA-100 instrument using approximately 5% solutions of the polymers in CDCl_3 with a CHCl_3 lock signal. Shifts from CHCl_3 have been translated to the δ -scale, using a nominal shift difference between tetramethylsilane and chloroform of 726 cycles. The spectra were virtually identical with a single 0.27-ppm chemical shift.

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