

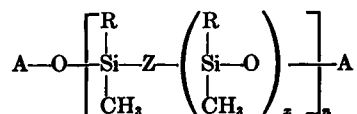
High-Temperature Elastomers: A Systematic Series of Linear Poly(Carborane-Siloxane)s Containing Icosahedral ($-\text{CB}_{10}\text{H}_{10}\text{C}-$) Cages.

II. Thermo-Oxidative Behavior

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Synopsis

A study of oxidative instability versus molecular structure 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



where (1) $x = 1, 3, 4, 5, \infty$; (2) A = endgroups (reactive and inert); (3) Z = *meta*-carborane, *para*-carborane (for $x = 3$); (4) R = $-\text{CH}_3$, R = $-\text{C}_2\text{H}_4\text{CF}_2$ (for $x = 3$), one in five R's = $-\text{C}_6\text{H}_5$ with the remainder $-\text{CH}_3$ (for $x = 4$); (5) molecular weight = $\sim 10,000, \sim 50,000$ (for $x = 3$). Thermomechanical spectra in air (~ 1 cps) from $130^\circ\text{C} \rightarrow 625^\circ\text{C} \rightarrow 130^\circ\text{C}$ at $3.6^\circ\text{C}/\text{min}$, thermogravimetric data from $25^\circ\text{C} \rightarrow 700^\circ\text{C}$ in air ($3.6^\circ\text{C}/\text{min}$), and differential thermal analysis data from $25^\circ\text{C} \rightarrow \sim 450^\circ\text{C}$ in air ($15^\circ\text{C}/\text{min}$) are presented. Thermo-oxidative stability is discussed in terms of structure, and broad categories of behavior are defined.

INTRODUCTION

The thermomechanical properties of a systematic series of molecularly well-characterized linear poly(carborane-siloxane)s containing icosahedral $-\text{CB}_{10}\text{H}_{10}\text{C}-$ cages have been recently reported.^{1,2} The reports included spectral identification (NMR and IR)² and melting, crystallization, glass and glassy state transitions¹ as determined by torsional braid analysis (TBA).³⁻⁵ A high degree of thermal stability (in nitrogen and argon) as detected by TBA, thermogravimetric analysis (TGA), and differential thermal analysis (DTA) was also reported.¹ The data indicated that in nitrogen, at a heating rate of $3.6^\circ\text{C}/\text{min}$, several of these materials did not crosslink or lose appreciable weight until temperatures

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greater than 500°C. This communication discusses the thermo-oxidative stability of the linear polymers in mechanical (by TBA) and thermal (by DTA and TGA) terms.

EXPERIMENTAL

Materials

The structures, nomenclature, and transitions of the linear carborane-siloxane polymers studied herein are shown in Table I.¹ Included also is a "pure" linear poly(dimethylsiloxane) silicone (SE-30, manufactured by the General Electric Company) which is designated 10-SiB-∞, the limiting structure of the 10-SiB-x series. Synthesis, work-up and molecular characterization have been described.^{1,2}

Techniques

The thermomechanical spectra (Figs. 1-3) were obtained by torsional braid analysis.³⁻⁵ The spectra, in flowing air, cover the temperature range of 130° to 625° to 130°C at a programming rate of 3.6°C/min.

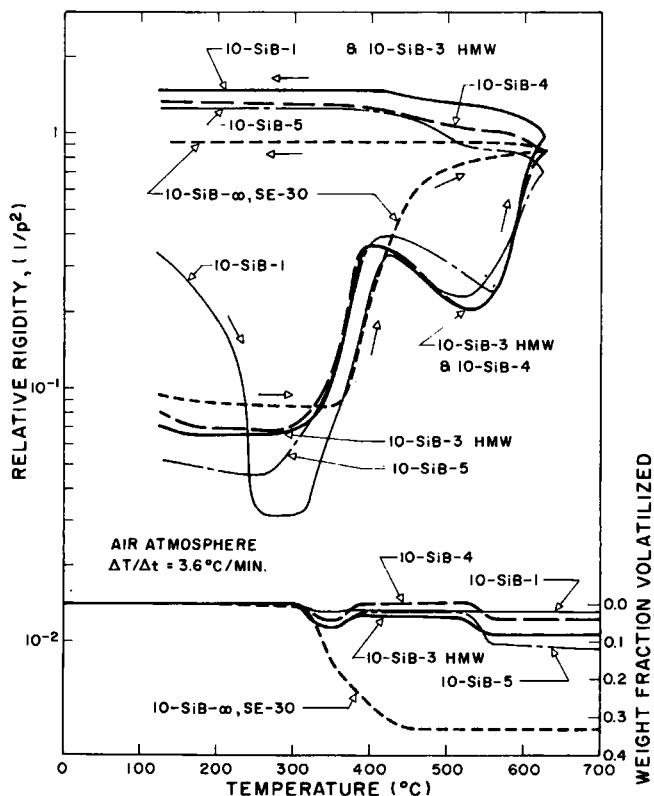


Fig. 1. Torsional braid and thermogravimetric analyses of 10-SiB-x polymers in air.

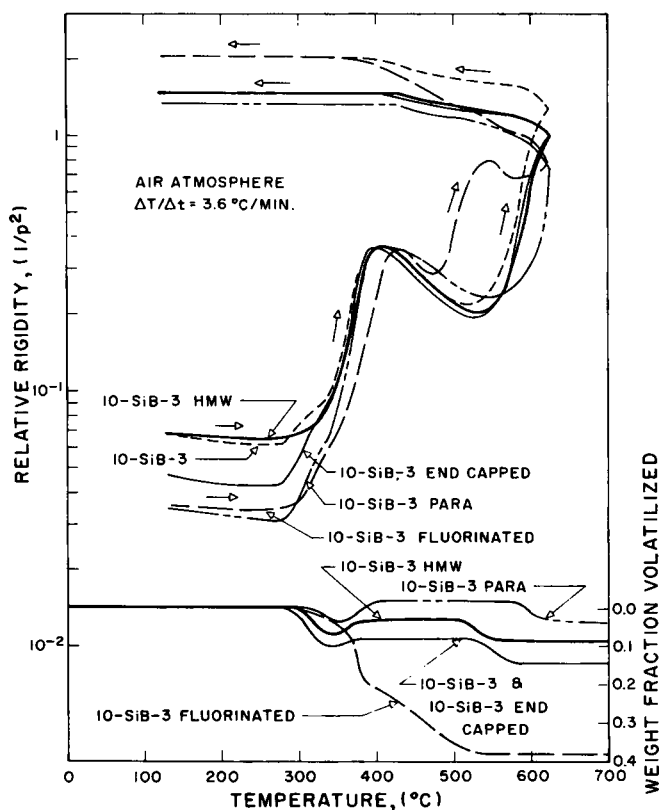


Fig. 2. Torsional braid and thermogravimetric analyses of 10-SiB-3 polymers in air.

The specimens were solvent-cast, glass braid/polymer composites. All specimens, except 10-SiB-1, were prepared by drying (in flowing nitrogen at 2°C/min) to 200°C a braid which had been soaked in a 10% (g polymer/ml solvent) solution of polymer in benzene. Since the 10-SiB-1 material was virtually insoluble in refluxing xylene, the composite specimen of it was prepared from a 5% slurry in refluxing xylene and was dried in nitrogen to 280°C at 2°C/min. In all cases, the drying cycle took the composite above the limiting solid-to-fluid transition (i.e., T_g or T_m) of the polymer and ensured a good coating on the filaments of the braid.

The TGA curves (Figs. 1-3) were generated on a du Pont Model 950 thermogravimetric analyzer and were run at 3.6°C/min. The specimens were cast from the same solutions and received the same thermal prehistories which were used to fabricate the mechanical specimens. Approximately 75 mg of solution were used for each run. Larger specimen weights (about 120 mg solution) gave somewhat different results (which will be discussed later).

The DTA curves (Figs. 4-6) were generated on a du Pont Model 900 thermoanalyzer. The heating rate was 15°C/min. The data were deter-

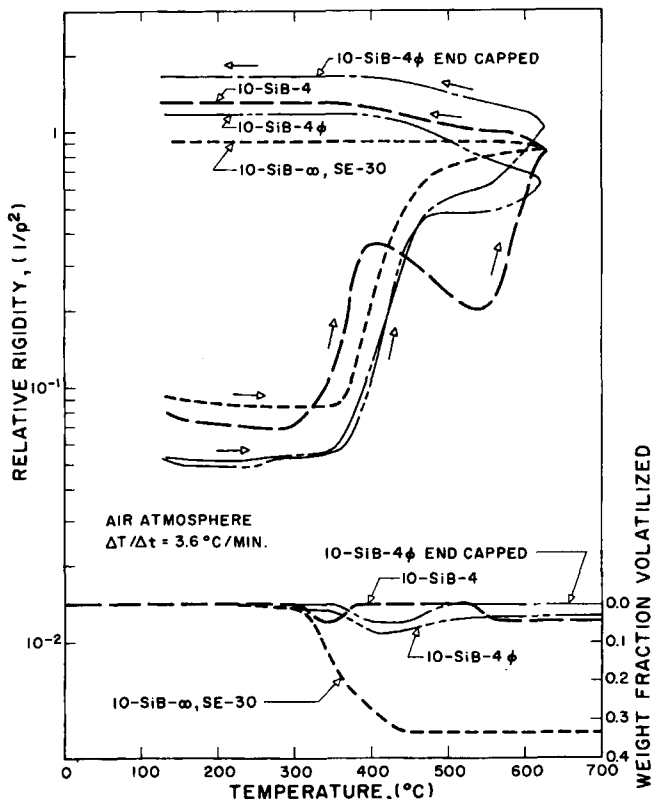


Fig. 3. Torsional braid and thermogravimetric analyses of 10-SiB-4 polymers in air.

mined on bulk specimens, "as received". The thermographs indicated no thermal events below the TBA maximum drying temperatures where all the polymers were fluids. The DTA, TGA, and TBA data correlated well.

Bottled inhalator air was used in all experiments (one cylinder for the mechanical work and one for the TGA and DTA work). The air was specified at 10 parts per million moisture.

RESULTS AND DISCUSSION

The 10-SiB-x Series

This series includes polymers I, IV, VII, XI, and XII of Table I. The TGA data and the TBA relative rigidity data are displayed in Figure 1; the DTA data are shown in Figure 4.

The 10-SiB-x TGA data indicate that, with the exception of pure silicone (10-SiB- ∞ , XII), the materials display a high degree of thermogravimetric stability. The onset of weight loss was about 300°C for all of the polymers. Pure silicone experienced virtually all of its weight loss below 400°C, which is the temperature corresponding to the onset of major

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	$HO \left[\begin{array}{c} CH_3 \\ \\ Si-CB_{10}H_{10}C-Si-O \\ \quad \\ CH_3 \quad CH_3 \end{array} \right]_n H$	260°C		230°C	25°C	-90°C 1.78
II 10-SiB-3	$HO \left[\begin{array}{c} CH_3 \quad CH_3 \\ \quad \\ Si-O-Si-CB_{10}H_{10}C-Si-O-Si-O \\ \quad \quad \quad \\ CH_3 \quad CH_3 \quad CH_3 \quad CH_3 \end{array} \right]_n H$ $[\eta]_{XYLENE} = 0.15-0.20 \text{ dl/g}$ GPC PEAK MAX. ~ 10-12,000	40		10	-68	-140 1.54
III 10-SiB-3 END-CAPPED	$CH_3-Si-O \left[\begin{array}{c} CH_3 \quad CH_3 \\ \quad \\ Si-O-Si-CB_{10}H_{10}C-Si-O-Si-O \\ \quad \quad \quad \\ CH_3 \quad CH_3 \quad CH_3 \quad CH_3 \end{array} \right]_n CH_3$ $[\eta]_{XYLENE} = 0.15-0.20 \text{ dl/g}$ MADE FROM II	40		10	-68	-140 → -145 1.54
IV 10-SiB-3 HIGH MW	$HO \left[\begin{array}{c} CH_3 \quad CH_3 \\ \quad \\ Si-O-Si-CB_{10}H_{10}C-Si-O-Si-O \\ \quad \quad \quad \\ CH_3 \quad CH_3 \quad CH_3 \quad CH_3 \end{array} \right]_n H$ $[\eta]_{XYLENE} = 0.65 \text{ dl/g}$ MW ~ 50-100,000	A		A	-70	-140
V 10-SiB-3 PARA	$HO \left[\begin{array}{c} CH_3 \quad CH_3 \\ \quad \\ Si-O-Si-C \begin{array}{c} \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \end{array} -CB_{10}H_{10}C-Si-O-Si-O \\ \quad \quad \quad \\ CH_3 \quad CH_3 \quad CH_3 \quad CH_3 \end{array} \right]_n H$ GPC PEAK MAX. ~ 15,000	110		90	-35	-115 1.61
VI 10-SiB-3 FLUORINATED	$HO \left[\begin{array}{c} CF_3 \quad CF_3 \\ \quad \\ Si-O-Si-CB_{10}H_{10}C-Si-O-Si-O \\ \quad \quad \quad \\ C_2H_4 \quad C_2H_4 \quad CH_3 \quad CH_3 \end{array} \right]_n H$ GPC PEAK MAX. ~ 8,500	A		A	-15	< -180 -90?
VII 10-SiB-4	$HO \left[\begin{array}{c} CH_3 \quad CH_3 \\ \quad \\ Si-O-Si-CB_{10}H_{10}C-Si-O-Si-O-Si-O \\ \quad \quad \quad \quad \\ CH_3 \quad CH_3 \quad CH_3 \quad CH_3 \quad CH_3 \end{array} \right]_n H$ GPC PEAK MAX. ~ 24,000	A		A	-75	-135
VIII 10-SiB-4 φ RANDOM	$HO \left[\begin{array}{c} CH_3 \quad CH_3 \\ \quad \\ Si-O-Si-CB_{10}H_{10}C-Si-O-Si-O \\ \quad \quad \quad \\ CH_3 \quad CH_3 \quad CH_3 \quad CH_3 \end{array} \right]_{0.5} \left[\begin{array}{c} C_6H_5 \\ \\ Si-O \\ \\ CH_3 \end{array} \right]_{0.5} H$ $\bar{M}_n = 12,000$ GPC PEAK MAX. ~ 15-20,000 RANDOM COPOLYMER	A		A	-58	-130 → -140
IX 10-SiB-4 φ	$HO \left[\begin{array}{c} CH_3 \quad CH_3 \\ \quad \\ Si-O-Si-CB_{10}H_{10}C-Si-O-Si-O-Si-O \\ \quad \quad \quad \quad \\ CH_3 \quad CH_3 \quad CH_3 \quad CH_3 \quad C_6H_5 \end{array} \right]_n H$ GPC PEAK MAX. ~ 12-18,000	A		A	-57	-140
X 10-SiB-4 φ END-CAPPED	$CH_3-Si-O \left[\begin{array}{c} CH_3 \quad CH_3 \\ \quad \\ Si-O-Si-CB_{10}H_{10}C-Si-O-Si-O-Si-O \\ \quad \quad \quad \quad \\ CH_3 \quad CH_3 \quad CH_3 \quad CH_3 \quad C_6H_5 \end{array} \right]_n CH_3$ GPC PEAK MAX. ~ 12-18,000 MADE FROM IX	A		A	-57	-140
XI 10-SiB-5	$HO \left[\begin{array}{c} CH_3 \quad CH_3 \quad CH_3 \\ \quad \quad \\ Si-O-Si-O-Si-CB_{10}H_{10}C-Si-O-Si-O-Si-O \\ \quad \quad \quad \quad \quad \\ CH_3 \quad CH_3 \quad CH_3 \quad CH_3 \quad CH_3 \quad CH_3 \end{array} \right]_n H$ GPC PEAK MAX. ~ 20,000	A		A	-88	-140
XII 10-SiB-∞ SE-30	$CH_3-Si-O \left[\begin{array}{c} CH_3 \\ \\ Si-O \\ \\ CH_3 \end{array} \right]_n CH_3$ MW > 10 ⁶	-40		-55	-125	A 1.58

A = absent.

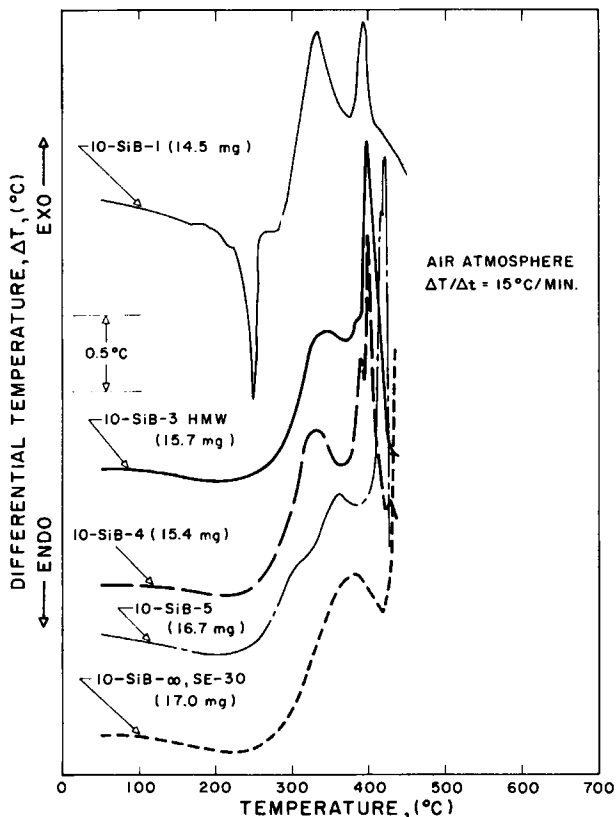


Fig. 4. Differential thermal analyses of 10-SiB-x polymers in air.

weight loss in an inert atmosphere.¹ All of the carborane polymers started to gain weight above about 350°C, and all but 10-SiB-1 lost weight again at about 525°C. The latter temperature corresponds to the only region of weight loss experienced by these materials in an inert atmosphere.¹ The weight loss curves were different when larger samples were used (about 120 mg). In each case, the increase in weight above 350°C did not occur, although all other features remained the same. Such dependences of reaction on surface to volume ratio is indicative of diffusion-controlled processes. It is of interest to note that there appears to be no simple relationship between the degree of weight loss above 600°C and the number of siloxane linkages per repeat unit. A linear relationship was found for the weight loss by 800°C in argon.¹ Polymer 10-SiB-1 appears to be the most and polymer 10-SiB-∞ the least oxidatively stable when examined by TGA.

The 10-SiB-x DTA data revealed the melting point for 10-SiB-1 as a sharp endotherm. Each 10-SiB-x polymer began to enter a broad exothermic peak in the range of 225° to 250°C. The peak occurred at higher temperatures with increasing content of siloxane groups in the repeat unit (with the exception of 10-SiB-4). A further sharp, well-defined exotherm

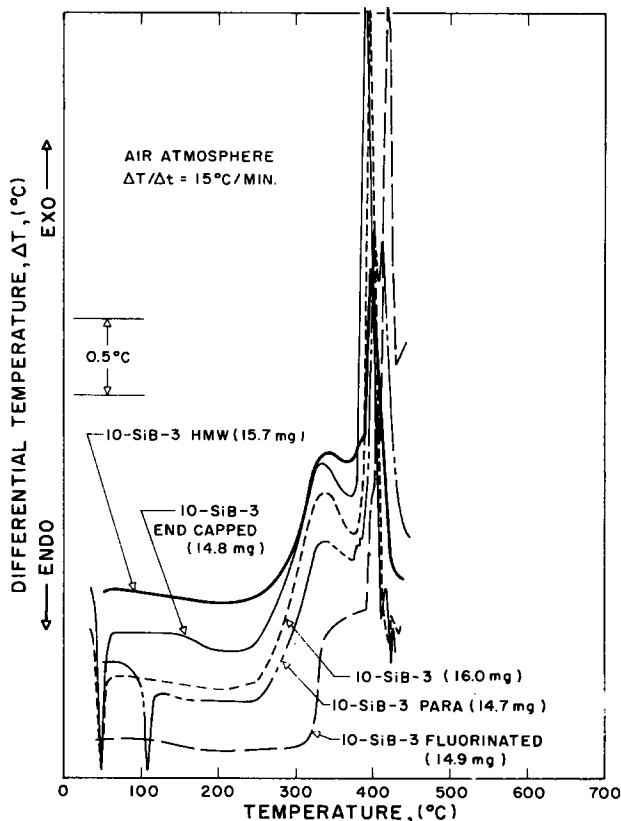


Fig. 5. Differential thermal analyses of 10-SiB-3 polymers in air.

was present between 390° and 425°C; the peak temperatures again increased with siloxane content. The data were erratic above approximately 430°C (not shown), indicating violent reactions.

The 10-SiB-*x* TBA relative rigidity curves are shown in Figure 1. The melting transition of 10-SiB-1 is responsible for the large drop in rigidity below 250°C. All of the carborane-containing polymers experienced a mode of stiffening near 300°C. The 10-SiB-1, -3, -4, and -5 polymers commenced stiffening at 300°, 290°, 290°, and 270°C, respectively. The 10-SiB-3, -4, and -5 polymers gave virtually identical stiffening plots from 300° to about 400°C, whereas 10-SiB-1 was shifted somewhat to higher temperatures (about 25°C). Examining the data from the point of view of the inflection point of the rigidity rise, all the carborane polymers had this point at about 360°C. Pure silicone was considerably more stable from an oxidative-mechanical point of view since it began to stiffen at about 350°C and had an inflection temperature of about 405°C. The rigidity decreased above 400°C for all the carborane-containing polymers, and above 540°C it increased again. The maximum in the rigidity curve would indicate either that there was a scission reaction competing successfully with the

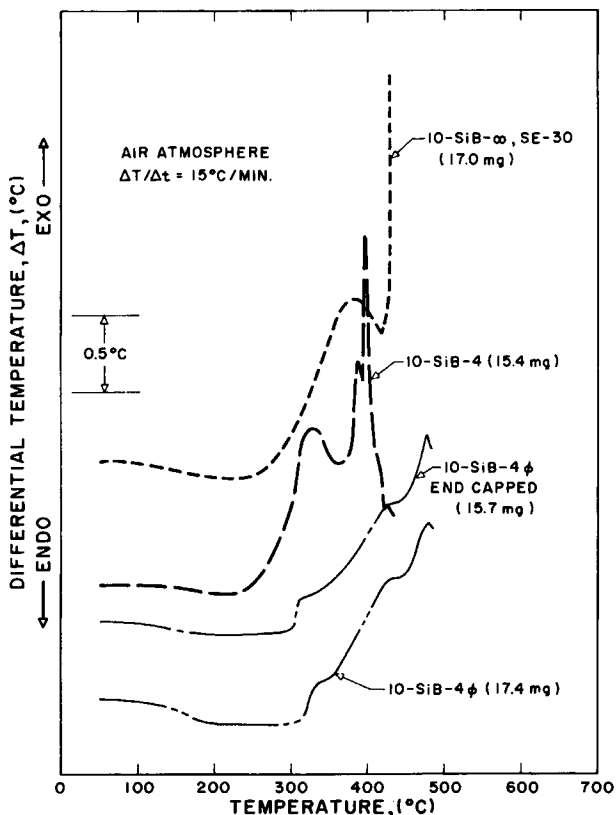


Fig. 6. Differential thermal analyses of 10-SiB-4 polymers in air.

stiffening reaction, or that the new material formed during the initial stiffening process was experiencing a physical transition (e.g., T_g). On the other hand, the pure silicone experienced only a one-stage stiffening process. The temperature for the maxima in rigidity for the carborane-containing polymers seems to correspond to the temperatures of the second exotherms observed by DTA in all cases except 10-SiB-1, for which the maximum in rigidity occurred at a higher temperature than the peak of the exotherm (420° versus 395°C). The coincidence of an exotherm with the onset of mechanical softening would indicate that a reactive softening mechanism is more likely than a physical one. All the oxidized carborane-containing polymers appeared to have broad glass transitions between 400° and 500°C on cooling from 625°C . [The differences in the levels of rigidity after curing to 625°C were dependent upon the different fractions of polymer on the braid (braid loading).] This type of behavior has been reported for other carborane-siloxane polymer systems which contained both B_{10} and B_5 cages.⁶ The 10-SiB-x polymers began to stiffen at about the same temperature as the 5-SiB-1 polymer previously reported,⁶ but at lower temperatures than the 5-SiB-1/20 mole-% 10-SiB-1 copolymer discussed

therein. Pure silicone appears to be the most oxidatively stable 10-SiB-x polymer by both DTA and TBA and yet the least stable by TGA studies.

The 10-SiB-3 Series

This series includes polymers II-VI of Table I. The TGA data and the TBA data are displayed in Figure 2; the DTA data are shown in Figure 5.

The 10-SiB-3 TGA data indicate that all of the all-methylated materials have a high degree of thermogravimetric stability and experienced the same type of multistep process which was observed in the 10-SiB-x series. The fluorinated polymer (VI) lost more than twice as much weight as the totally methylated polymers, with the first major weight loss region commencing near 300°C and reached the highest rate at about 350-375°C. The second weight loss region for the same polymer began at about 380°C and continued until about 525°C. As in the 10-SiB-x series, the all-methylated materials commenced weight loss at about 300°C. The 10-SiB-3 *para*-carborane polymer had a final weight loss that was less than that for the *meta*-carborane polymers, and its second stage of weight loss occurred about 40°C higher. The second stage of weight loss in air for the all-methylated *meta*-10-SiB-3 and *para*-10-SiB-3 polymers occurred at about the same temperature as did the single staged weight losses in argon.¹ The different weight loss levels for the all-methyl polymers (IV vs. II and III) are probably due to different average molecular weights and molecular weight distributions.¹ The *para*-10-SiB-3 appears to be the most oxidatively stable of the 10-SiB-3 polymers when studied by TGA.

All of the 10-SiB-3 DTA data are very much like those for the 10-SiB-x series. The melting points (T_m) of II, III, and V were revealed by sharp endotherms at 47°, 47°, and 108°C and correspond to the reported values.¹ A two-stage process commencing between 225° and 250°C was indicated for all polymers, except for the fluorinated polymer, which entered its first exotherm at about 300°C. The first peak of the exotherm for the fluorinated material was flatter than for the other 10-SiB-3 polymers, and the second exotherm peaked at 440° rather than 390° to 410°C. The fluorinated material appears more oxidatively stable than the other 10-SiB-3 polymers when examined by DTA.

The 10-SiB-3 TBA data are almost identical in form to those of the 10-SiB-x series, except for the fluorinated polymer. The all-methylated polymers experience the initial stiffening at about 280°C and a maximum near 400°C. The behavior of the fluorinated polymer was similar, except that the line of increase of rigidity was shifted to higher temperatures by about 25°C, and the maximum was at about 430°C. The all-methylated materials experienced a decrease in rigidity after the maximum and then stiffened again. The *para*-carborane polymer experienced the second stiffening (and second weight loss) about 40°C higher. The fluorinated polymer experienced a second maximum indicating an additional stiffening/softening process. The second increase in rigidity in air for all of these carborane-containing polymers occurred at temperatures which corre-

sponded to drastic increases in rigidity in nitrogen.¹ All the materials again displayed a T_g region in the 400° to 500°C range on cooling from 625°C, as was observed for the 10-SiB-x series. A ranking of thermo-mechanical oxidative stability is difficult to define within this series.

The 10-SiB-4 Series

This series includes polymers VII, IX, and X (VIII was not studied oxidatively; pure silicone, XII, is shown for comparison). The TGA data and the TBA data are displayed in Figure 3; the DTA data are shown in Figure 6.

The 10-SiB-4 TGA data indicate a higher degree of thermogravimetric oxidative stability relative to the 10-SiB-x and 10-SiB-3 series of polymers. The phenylated polymers (IX and X) displayed small total weight losses by 800°C and displayed their major mode of weight loss commencing at 350°C rather than at 300°C as for the all-methylated 10-SiB-4 (VII). All three 10-SiB-4 polymers displayed a weight gain (at 350°C for VII and at 430°C for IX and X), and the phenylated polymers displayed a broader region of weight gain. Only the totally methylated 10-SiB-4 experienced the second mode of weight loss common to the methylated polymers discussed above. In the 10-SiB-4 series, the phenylated polymers are the most thermogravimetrically stable in air.

The 10-SiB-4 DTA data amplify the TGA results. Whereas the all-methylated 10-SiB-4, VII, entered an exothermic region at about 240°C, the phenylated polymers, IX and X, entered such a region at 300° and 290°C, respectively. The exotherms themselves reflected the less abrupt nature of the weight loss for the phenylated polymers. The exothermic peaks for the methylated 10-SiB-4 polymer were sharp, whereas those for the phenylated polymers were broad and diffuse. The DTA data indicate high stability for the phenylated versus the totally methylated 10-SiB-4 polymers, both from the point of view of the onset of the oxidative exotherm and of the sharpness of the reaction region.

The 10-SiB-4 TBA data in Figure 3 include the plot of the 10-SiB-∞ curve for purposes of comparison. The following ranking can be established for the three classes of materials in this figure. The phenylated carborane-siloxane polymers and the pure silicone are significantly more stable than the totally methylated 10-SiB-4 when monitored thermo-mechanically in air. Other interesting features are the 10°C difference in the onset of catastrophic stiffening of the end-capped versus non-end-capped phenylated polymers (the end-capped reacts first, as was also detected via DTA) and the nonsoftening of the phenylated polymers above 400°C. This second feature is of interest since the two-stage stiffening process was still evident. The phenylated materials appear to be more highly crosslinked than the other polymers (in all series) after the first stiffening process. This is apparent since all the other rigidity curves displayed very nearly the same numerical value for relative rigidity at their

respective maxima regardless of their braid loading. This excess crosslink density may be due to the 430°C stiffening observed thermomechanically in nitrogen at the same programming rate but not observed for the methylated polymers. On the other hand, the second stage of stiffening in all of the polymers which displayed a two-stage stiffening process occurred near the temperature region (530° to 570°C) of catastrophic stiffening in nitrogen.¹

The damping-versus-temperature curves for the thermomechanical behavior in air are not shown herein because the data did no more than reflect the information derived from the rigidity plots. In general terms each damping curve displayed a damping peak corresponding to each stage of the multistaged stiffening region. On cooling from 625°C, a large drop in damping occurred at about 400°C. The overall damping behavior was similar to that in air of the 5-SiB-1 polymers previously reported.⁶ Several of the materials which began to stiffen below 300°C displayed a damping peak at the onset of stiffening and another one in the region of catastrophic stiffening. The others displayed only one peak corresponding to the first reaction region. Both types displayed further peaks at higher temperatures corresponding to stiffening during later stages of reaction.

CONCLUSIONS

The thermo-oxidative studies discussed above, indicate that the poly(carborane-siloxane)s listed in Table I fall into two classes of thermomechanical degradation. The first class is composed of all the totally methylated carborane-containing polymers (I-VII and XI) and is defined by the 280° to 300°C temperature region for the onset of stiffening. This oxidation temperature corresponds well to the 275°C oxidation temperature recently reported for cured 10-SiB-3 at a heating rate of 1°C/min.⁷ The second class, defined by onset of stiffening at about 350°C, is composed of pure silicone (XII) and the phenylated carborane-containing polymers (IX and X). Examination of the TGA data for pure silicone would discount any advantage derived from the increased temperature of onset of stiffening, while the TGA data for the phenylated materials would indicate a high degree of relative utility. This raises the interesting possibility of making *crosslinked* poly(dimethylsiloxane) materials that are inherently more oxidatively stable than their poly(carborane-siloxane) counterparts so long as the crosslinks are not the weak links. The multi-step nature of the TBA data for all of the carborane-containing polymers and the coincidence of the second increase in rigidity in air with the catastrophic increases in nitrogen indicated that the response of the polymers in air was a combination of oxidative and thermal events that could be separated upon examination of previously reported thermomechanical data.¹ The rather close grouping of the curves within each of the two reaction regions has prompted the authors to consider isothermal oxidative

studies to better define the close ranking of the materials in each class and to determine activation energies for the stiffening processes.

It is of interest to note that with respect to thermomechanical stability, the incorporation of carborane cages into siloxane backbones decreases the threshold of oxidative stiffening. Related work reported recently in the Soviet literature⁸ indicated that the incorporation of *meta*-carborane cages into polyamido backbones resulted in the formation of B₂O₃ upon long-term exposure to air at 230–250°C. The nature of the stiffening processes for the pure silicone (one step) as compared to the carborane-containing polymers (multistep), and the transition behavior of the oxidatively cured (to 625°C) materials ($T_g > 625^\circ\text{C}$ for the silicone; $T_g = 400\text{--}500^\circ\text{C}$ for the carborane polymers) further indicate that the carborane cage itself has some direct effect on the oxidation process. Future work to determine the chemical structure of the pyrolytic products of oxidation is planned in order to provide a better understanding of the degradation mechanisms.

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