

## High-Temperature Elastomers: Glass Transition-Structure Correlations for Two Systematic Series of Linear Poly(Carborane-Siloxane)s. I

M. B. ROLLER\* and J. K. GILLHAM, *Polymer Materials Program, Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08540*

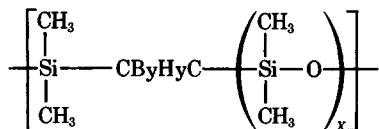
### Synopsis

Nine linear poly(carborane-siloxane) high-temperature elastomers which differ systematically in chemical structure were investigated by torsional braid analysis. The structural variations include two different carborane cage structures in the polymer chain ( $-\text{CB}_{10}\text{H}_{10}\text{C}-$  and  $-\text{CB}_5\text{H}_5\text{C}-$ ) and the stepwise increase in the number of  $-\text{Si}(\text{CH}_3)_2-\text{O}-$  linkages associated with each cage in the repeat unit. Poly(dimethylsiloxane) was studied as the compositional limit of both series. The dynamic mechanical relaxations (at about 1 cps) of the materials are reported. These include the melting points of the semicrystalline polymers and the glass transitions and secondary transitions of all the polymers. The glass transition temperatures in each series were systematized using the well-known copolymer composition-versus-glass transition temperature relationship  $1/T_g = W_1/T_{g1} + W_2/T_{g2}$ .

### INTRODUCTION

The search for high-temperature elastomers has led to the development and marketing of the carborane-siloxane polymers.<sup>1-5</sup> Most of the work to date has involved synthesizing copolymers with the ten-boron-containing meta-carborane cage (Fig. 1A) replacing a definite fraction of oxygen atoms in a dimethylsiloxane backbone. Polymers containing the ten-boron cage are represented by structures I to IV, Table I. Carborane nuclei with five boron atoms per cage have been incorporated recently into linear poly(carborane-siloxane)s. Polymers containing the five-boron cage (Fig. 1B) are represented by structures VI to X, Table II.

The basic structure,



is designated Y-SiB-X.

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

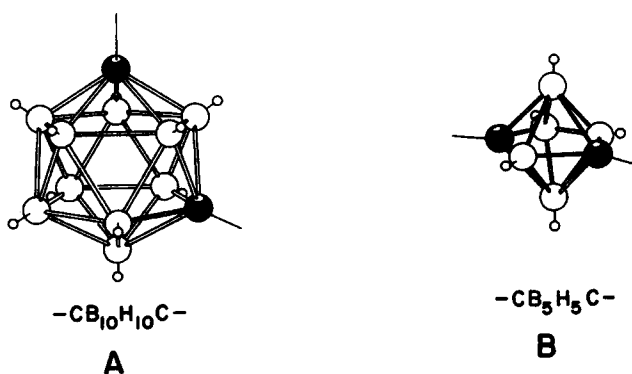


Fig. 1. (A)  $\text{B}_{10}$  carborane cage; (B)  $\text{B}_5$  carborane cage.

The linear 10-SiB-X series, with  $X = 1, 3, 4, 5,$  and  $\infty$ , was synthesized and molecularly characterized at the Olin Research Center, New Haven, Connecticut. The syntheses were such that each ten-boron cage would be expected to be regularly positioned along the backbone, replacing every  $(X + 1)$ th oxygen atom of a polysiloxane chain.<sup>6,7</sup> The regularity of the structures has been confirmed using NMR spectra.<sup>6,7</sup>

The linear 5-SiB-X series was synthesized by Chemical Systems Incorporated, Santa Ana, California. For these polymers, the syntheses were such that the composition of each polymer corresponded to the overall composition 5-SiB-X ( $X = 2, 3, 4, 5$ ). The comonomer residues were those of 5-SiB-1 and 5-SiB- $\infty$  [poly(dimethylsiloxane), Table II, compound XI] as is indicated in the structures of Table II. The structures are believed to be random.<sup>8,9</sup> The 5-SiB-1 polymer was obtained by a condensation procedure<sup>10</sup> that insured the regular structure. Although the number-average molecular weights of the 5-SiB-2, 5-SiB-3, 5-SiB-4, and 5-SiB-5 materials were very low by "rule of thumb" standards (10,000 for high-polymer behavior), the materials were either elastic gum rubbers or highly viscous and elastic fluids at room temperature. By contrast, linear poly-(dimethylsiloxane) gums designed to display rubbery character generally have molecular weights greater than 500,000.<sup>11</sup> Past experience with similar materials (5-SiB-1 copolymerized with 20 mole-% 10-SiB-1) indicated that changing the number-average molecular weight from 3800 to 11400 has no effect on the transition temperatures.<sup>12</sup>

## EXPERIMENTAL

The transition data presented in Tables I and II were determined in dried nitrogen by the technique of torsional braid analysis (TBA),<sup>13-16</sup> which employs a modified torsional pendulum operating at about 1 cps. The torsional braid analyzer is a free-hanging torsional pendulum. The specimen consists of a multifilamented (about 3600) glass braid impregnated with the sample polymer, allowing the study of semimicro quantities (<50 mg).

TABLE I  
Chemical Formulae and Transitions of 10-SiB-X Polymers

DESIGNATION	STRUCTURE	T <sub>m</sub>	T <sub>c, DSC</sub>	T <sub>g</sub>	T <sub>sec</sub>	T <sub>m</sub> /T <sub>g</sub>
I 10-SiB-1	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{HO}-\text{Si}-\text{CB}_{10}\text{H}_{10}\text{C}-\text{Si}-\text{O}-\text{H} \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n$	260°C	n.a.	25°C	-90°C	1.78
II 10-SiB-3	$\left[ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{HO}-\text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10}\text{C}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{H} \\   \quad   \quad   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n$ <p><math>[\eta]_{\text{XYLENE}} = 0.15-0.20 \text{ dl/g}</math> GPC PEAK MAX. ~10-12,000</p>	40	10	-68	-140	1.54
III 10-SiB-4	$\left[ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{HO}-\text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10}\text{C}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{H} \\   \quad   \quad   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n$ <p>GPC PEAK MAX. ~24,000</p>	A	A	-75	-135	
IV 10-SiB-5	$\left[ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{HO}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{CB}_{10}\text{H}_{10}\text{C}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{H} \\   \quad   \quad   \quad   \quad   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n$ <p>GPC PEAK MAX. ~20,000</p>	A	A	-88	-140	
V 10-SiB-∞ SE-30	$\left[ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{CH}_3-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{O}-\text{Si}-\text{CH}_3 \\   \quad   \quad   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n$ <p>MW &gt; 10<sup>6</sup></p>	-40	-55	-125	A	1.58

A = ABSENT  
n.a. = NOT AVAILABLE

TABLE II  
Chemical Formulae and Transitions of 5-SiB-X Polymers

DESIGNATION	STRUCTURE	$T_m$	$T_{cryst}$	$T_g$	$T_{sec}$	$T_m/T_g$
VI 5-SiB-1	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{HO}-\text{Si}-\text{C}_6\text{H}_5-\text{C}-\text{Si}-\text{O}-\text{H} \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n$ $\bar{M}_n = 12,500 \pm 10\%$	70°C	50°C	-60°C	-140°C	1.61
VII 5-SiB-2 RANDOM COPOLYMER	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{HO}-\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{C}_6\text{H}_5-\text{C}-\text{Si}-\text{O}-\text{H} \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_f \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{O}-\text{H} \\   \\ \text{CH}_3 \end{array} \right]_g \end{array} \right]_n$ $\bar{M}_n = 6170 \pm 10\%$	A	A	-88	-145	
VIII 5-SiB-3 RANDOM COPOLYMER	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{HO}-\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{C}_6\text{H}_5-\text{C}-\text{Si}-\text{O}-\text{H} \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_f \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{O}-\text{H} \\   \\ \text{CH}_3 \end{array} \right]_g \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{O}-\text{H} \\   \\ \text{CH}_3 \end{array} \right]_h \end{array} \right]_n$ $\bar{M}_n = 5860 \pm 10\%$	A	A	-96	-145	
IX 5-SiB-4 RANDOM COPOLYMER	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{HO}-\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{C}_6\text{H}_5-\text{C}-\text{Si}-\text{O}-\text{H} \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_f \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{O}-\text{H} \\   \\ \text{CH}_3 \end{array} \right]_g \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{O}-\text{H} \\   \\ \text{CH}_3 \end{array} \right]_h \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{O}-\text{H} \\   \\ \text{CH}_3 \end{array} \right]_i \end{array} \right]_n$ $\bar{M}_n = 4270 \pm 10\%$	A	A	-102	-140	
X 5-SiB-5 RANDOM COPOLYMER	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{HO}-\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{C}_6\text{H}_5-\text{C}-\text{Si}-\text{O}-\text{H} \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_f \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{O}-\text{H} \\   \\ \text{CH}_3 \end{array} \right]_g \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{O}-\text{H} \\   \\ \text{CH}_3 \end{array} \right]_h \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{O}-\text{H} \\   \\ \text{CH}_3 \end{array} \right]_i \left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{O}-\text{H} \\   \\ \text{CH}_3 \end{array} \right]_j \end{array} \right]_n$ $\bar{M}_n = 3920 \pm 10\%$	A	A	-108	-145	
XI 5-SiB- $\infty$ SE-30	$\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{Si}-\text{O}-\left[ \begin{array}{c} \text{CH}_3 \\   \\ \text{Si}-\text{C}_6\text{H}_5-\text{C}-\text{Si}-\text{CH}_3 \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array} \right]_n \text{CH}_3 \\   \\ \text{CH}_3 \end{array} \right]_n$ $\text{MW} > 10^6$	-40	-55	-125	A	1.58

A = ABSENT

The specimen is fabricated in situ to form a glass-polymer composite, by removing solvent from a braid that has been soaked in a polymer solution prior to mounting. The composite nature of the specimen has the further advantage of allowing room-temperature handling of materials that are gums or viscous fluids at room temperature. The glass braid carries the tensile stress in the specimen. The transitions of the polymers are readily determined by monitoring changes in the dynamic rigidity modulus and mechanical damping of the specimen as a function of temperature.

## RESULTS

In the 10-SiB-X series, where  $X = 1, 3, 4, 5$ , and  $\infty$  [infinity corresponds to pure poly(dimethylsiloxane)], the glass transition temperatures are  $25^\circ$ ,  $-68^\circ$ ,  $-75^\circ$ ,  $-88^\circ$ , and  $-125^\circ\text{C}$ , respectively. For  $X = 3, 4$ , and  $5$ , there is a secondary transition ( $T_{\text{sec}}$ ) in the vicinity of  $-135^\circ$  to  $-140^\circ\text{C}$ . The 10-SiB-1 polymer has a  $T_{\text{sec}}$  at  $-90^\circ\text{C}$ , while 10-SiB- $\infty$  (compound V, Table I) displays no apparent secondary transition above  $-180^\circ\text{C}$  (this may be due to the low glass transition temperature which results in merging of the  $T_g$  damping peak and a low intensity glassy-state damping peak). For  $X = 1$  ( $T_m = 260^\circ\text{C}$ ),  $X = 3$  ( $T_m = 40^\circ\text{C}$ , slightly crystalline), and  $X = \infty$  ( $T_m = -40^\circ\text{C}$ ), the polymers are crystalline. For  $X = 3$ , a higher molecular weight sample ( $[\eta]_{\text{xylene}} = 0.65$  dl/g) was available which was not semicrystalline ( $T_g = -70^\circ\text{C}$ ,  $T_{\text{sec}} = -140^\circ\text{C}$ ).<sup>17</sup>

The lower line of Figure 2 is a plot of  $1/T_g$  versus  $W_1$ , where  $W_1 =$  weight fraction of  $-\text{Si}(\text{CH}_3)_2-\text{CB}_{10}\text{H}_{10}\text{C}-$  in the polymer repeat unit. If the copolymer equation<sup>18,19</sup>

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

is applied to this alternating copolymer system, where the subscript 2 refers to  $-\text{Si}(\text{CH}_3)_2-\text{O}-$ , the data should lie on a straight line. The 10-SiB-3, 4, 5, and  $\infty$  data fall well on a straight line. The  $X = 2$  data (two points) were reported<sup>20</sup> for slightly crystalline and crosslinked 10-SiB-2 and are off the line. The higher  $T_g$  value for  $X = 2$  was determined as a 10-second modulus by stress relaxation techniques, the lower  $T_g$  value, by volume-temperature studies. The 10-SiB-2 material is reported to be obtained from bulk copolymerization of dichlorodimethylsilane and 1,7-bis(methoxydimethylsilyl)-*m*-carborane monomers, which form chains approaching 10-SiB-2 in overall composition. The material obtained is a crystalline crosslinked gum containing cyclic and linear oligodimethylsiloxanes ( $-\text{Si}(\text{CH}_3)_2-\text{O}-$ ) and some 10-SiB-1 oligomers.<sup>21</sup> The formation of crosslinks was inherent to the reaction, and additional side reactions (e.g., redistribution) were suspected to have occurred. The random structure relative to the other 10-SiB-X polymers, the unaccounted-for side reactions, the crystallinity, and the crosslinks, all lend a degree of understanding to the polymer's deviation from the proposed straight line. However, the 10-SiB-1 polymer deviates even more from the trend established

for the  $X = 3, 4, 5,$  and  $\infty$  polymers. The value  $T_g = -7^\circ\text{C}$  predicted by the straight line is  $32^\circ\text{C}$  lower than the value of  $25^\circ\text{C}$  determined mechanically via TBA (and also previously reported<sup>22</sup> for vulcanized and filled 10-SiB-1). The unusually high glass transition is accompanied by a value for  $T_{\text{sec}}$  of  $-90^\circ\text{C}$ , which is high compared with the value of about  $-140^\circ\text{C}$  measured for the other 10-SiB- $X$  polymers and the several 5-SiB- $X$  polymers discussed below. The  $T_m/T_g$  ratio of 1.78 (see Table I) for 10-SiB-1 is considerably higher than the values for the 10-SiB-3 and the highly symmetrical 10-SiB- $\infty$  [poly(dimethylsiloxane)].

The relatively high value for the glass transition of 10-SiB-1 is of interest and merits discussion. The polymer is highly crystalline and barely soluble ( $<1\%$  in hot xylene) and was difficult to purify. One would expect any impurities in the polymer to lower the value of  $T_g$  (and especially  $T_m$ , and thereby  $T_m/T_g$ ), not to raise it. The "ball and chain" configuration of the 10-SiB- $X$  polymers raises the question as to whether the solid state properties, as determined by intramolecular and intermolecular factors 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. If a simple calculation is made for 10-SiB-1, by taking the volume of the carborane cage as being equal to the volume of the sphere circumscribing a regular icosahedron of side  $1.75 \text{ \AA}$  (the dimension of the edge of the cage structure, ignoring hydrogen atoms)<sup>23</sup> and by taking the volume of the  $-\text{Si}(\text{CH}_3)_2-\text{O}-\text{Si}(\text{CH}_3)_2-$  group as being the sum of the volumes of the covalently bonded atoms (ignoring hydrogen atoms), then the  $-\text{CB}_{10}\text{H}_{10}\text{C}-$  cage is 0.52 of the sum of the two parts. In a simple cubic array of touching balls (one ball at each corner of a cube, the side of the cube being equal to the diameter of a ball), the fractional void volume not occupied by the balls is 0.476; the balls occupy a 0.524 fraction of the cube. This could suggest that packing of carborane cages is a major determinant of properties for the 10-SiB-1 polymer. These numbers should be viewed only as a qualitative measure of the possible microscopic packing of carborane cages themselves. The analysis is, of course, limited by the approximations stated above and the disregard of the limitations imposed by bonding angles. This association effect, and/or the crystallinity and cross-linking of the 10-SiB-2 sample, may also contribute to the latter's higher-than-expected glass transition.

Carrying the extrapolation of the copolymer equation one step further, a glass transition temperature of  $103^\circ\text{C}$  is predicted for the 10-SiB-0 polymer with repeat structure  $(-\text{Si}(\text{CH}_3)_2-\text{CB}_{10}\text{H}_{10}\text{C}-)$ , in the absence of any complicating factors. This 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<sup>23</sup>). The character of the  $\text{Si}-\text{C}_{\text{carborane}}$  bond is unusual in that there must be a high facility for torsional oscillations of the bond in spite of the large size of the carborane cage.

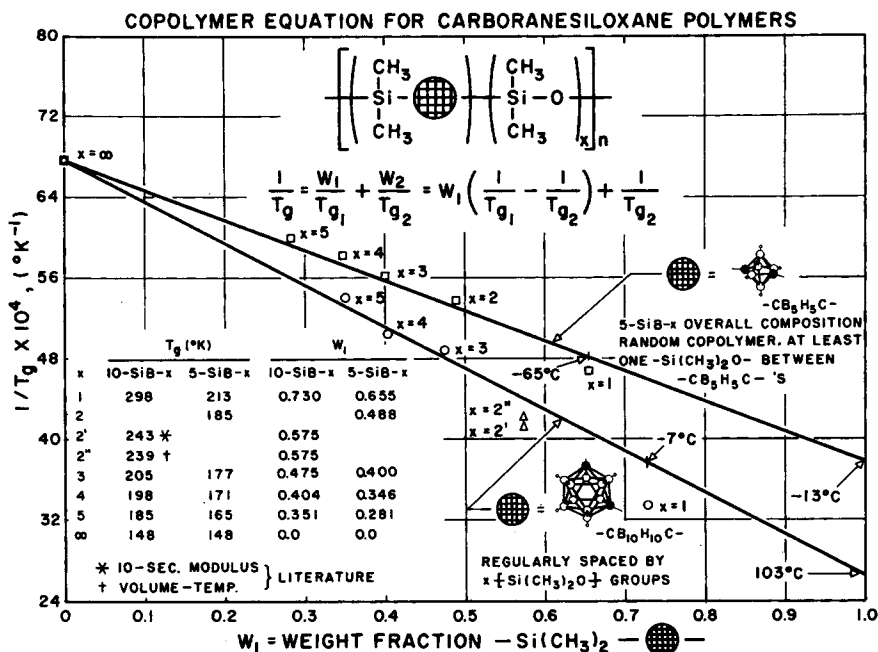


Fig. 2. Copolymer equation. Glass transition temperature-structure correlations for 10-SiB-X and 5-SiB-X polymers.

In the 5-SiB-X series, where  $X = 1, 2, 3, 4, 5$ , and  $\infty$ , the glass transition temperatures are  $-60^\circ$ ,  $-88^\circ$ ,  $-96^\circ$ ,  $-102^\circ$ ,  $-108^\circ$ , and  $-125^\circ\text{C}$ , respectively. All of these polymers except one ( $X = \infty$ ) have a secondary transition at about  $-140^\circ\text{C}$ . The 5-SiB- $\infty$  (SE-30) polymer was discussed above. It should be noted that 5-SiB- $\infty$  (compound XI) and 10-SiB- $\infty$  (compound V) are identical but are separately listed as the limit of each series. The 5-SiB-1 ( $T_m = 70^\circ\text{C}$ ) and the 5-SiB- $\infty$  polymer ( $T_m = -40^\circ\text{C}$ ) were crystalline.

Referring to Figure 2 again, the upper line is a plot of  $1/T_g$  versus  $W_1$ , where  $W_1$  = weight fraction of  $-\text{Si}(\text{CH}_3)_2-\text{CB}_5\text{H}_5\text{C}-$  in the polymer chain. The data should fall on a straight line. This is the case, but the fit is considerably better than for the 10-SiB-X series. The extrapolated glass transition temperature of  $-65^\circ\text{C}$  for 5-SiB-1 is only  $5^\circ\text{C}$  different from the experimental value, in spite of the crystalline nature of the material. The further extrapolation to  $W_1 = 1.0$  (corresponding to 5-SiB-0) predicts a glass transition temperature of  $-13^\circ\text{C}$ .

The very good fit of the 5-SiB-X data indicates that the mechanism of cage-cage impingement is not as active in the 5-SiB-X series. The smaller cage and/or a more flexible 5-SiB-X versus 10-SiB-X carbon<sub>carborane</sub>-silicon bond tend to lower the glass transition temperature for a given X. For example, 5-SiB-1 corresponds to 10-SiB-3, and 5-SiB-2 corresponds to 10-SiB-5. The extrapolated value of  $-13^\circ\text{C}$  for a 5-SiB-0 material is noteworthy since the replacement in the poly(dimethylsiloxane) repeat

unit of two flexible Si-O bonds by two Si-C bonds coupled with the replacement of a small —O— atom by a large cage structure might be expected to produce a stiff polymer backbone.

## CONCLUSIONS

The copolymer equation formulated<sup>18,19</sup> as

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

is highly successful in correlating the glass transitions of two systematic series of linear carborane-siloxane polymers. The relationship appears to correlate equally well the data for both an alternating copolymer system, 10-SiB-X, and a random copolymer system, 5-SiB-X. The constantly lower temperature for a given molar composition and the less steep slope of the 5-SiB-X curve relative to the 10-SiB-X curve indicate that the five-boron cage is less effective in stiffening the polymer chain than the ten-boron cage. This is not unexpected in view of steric considerations since the ten-boron cage structure has approximately twice the volume of the five-boron cage structure. The fact that substituents as bulky as these do not have greater effect when replacing the very flexible Si-O-Si bond is noteworthy. A highly flexible C<sub>carborane</sub>-Si bond must be present in order to maintain the chain flexibility. It is likely that in consequence of the different degrees of delocalization of electrons in the two cage structures (ten-boron versus five-boron), the C-Si bonds are significantly different and so complement the steric effects already considered.

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## References

1. S. Papetti, B. B. Schaeffer, A. P. Gray, and T. L. Heying, *J. Polym. Sci. A-1*, **4**, 1623 (1966).
2. H. A. Schroeder, O. G. Schaffling, T. B. Larchar, F. F. Frulla, and T. L. Heying, *Rubber Chem. Technol.*, **39**, 1184 (1966).
3. H. A. Schroeder, *Rubber Age*, **101**, 58 (1969).
4. H. A. Schroeder, *Inorg. Macromol. Rev.*, **1**, 45 (1970).
5. D. J. Mangold, *Appl. Polym. Symposia*, **11**, 157 (1969).
6. K. O. Knollmueller, R. N. Scott, H. Kwasnik, and J. F. Sieckhaus, *J. Polym. Sci. A-1*, **9**, 1071 (1971).
7. J. F. Sieckhaus, private communication.
8. R. E. Kesting, K. F. Jackson, and J. M. Newman, *J. Appl. Polym. Sci.*, **15**, 2645 (1971).
9. R. E. Kesting, letter to J. K. Gillham dated Sep. 15, 1971.
10. R. E. Kesting, K. F. Jackson, E. B. Klusmann, and F. J. Gerhart, *J. Appl. Polym. Sci.*, **14**, 2525 (1970).
11. R. N. Meals, *Silicones in Encyclopedia of Chemical Technology*, Vol. 18, 2nd ed. Wiley, New York, 1969, p. 221.
12. M. B. Roller and J. K. Gillham, *J. Appl. Polym. Sci.*, **16**, 3073 (1972).



13. A. F. Lewis and J. K. Gillham, *J. Appl. Polym. Sci.*, **6**, 422 (1962).
14. J. K. Gillham, *Polym. Eng. Sci.*, **7**, 225 (1967).
15. J. K. Gillham and M. B. Roller, *Polym. Eng. Sci.*, **11**, 295 (1971).
16. J. K. Gillham, *Torsional Braid Analysis*, in *Encyclopedia of Polymer Science and Technology*, Vol. 14, Interscience, New York, 1971, p. 76.
17. M. B. Roller, and J. K. Gillham, *Preprints, Div. Polym. Chem., Amer. Chem. Soc.*, **13**, 227 (1972).
18. T. G. Fox, *Bull. Amer. Phys. Soc.*, **1**, 123 (1950).
19. L. A. Wood, *J. Polym. Sci.*, **28**, 319 (1958).
20. L. H. Sperling, S. L. Cooper, and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **10**, 1725 (1966).
21. H. J. Dietrich, R. P. Alexander, T. L. Heying, H. Kwasnik, C. O. Obenland, and H. A. Schroeder, *Icosahedral Carboranes. XVI. Polymerization and Crosslinking Mechanism of Polym-carboranylenesiloxanes*. ONR Contract 3395 (00), Tech. Report No. 45, 1970.
22. E. J. Zaganianis, L. H. Sperling, and A. V. Tobolsky, *J. Macromol. Sci.-Chem.*, **A1(6)**, 111 (1967).
23. E. L. Mutterties and W. H. Knoth, *Polyhedral Boranes*, Marcel Dekker, New York, 1968, pp. 21-28.

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