

## The Introduction of Elastomeric Behavior into Polycarboranylenesiloxane SiB-1 Polymers from the *Closo*-carborane $C_2B_5H_7$

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### Synopsis

The copolymerization of a small amount of the larger ( $C_2B_8$  and  $C_2B_{10}$ ) carboranes with the smaller  $C_2B_5$  carborane resulted in the formation of an elastomeric SiB-1 carborane-siloxane, a polymer hitherto prepared only in crystalline form. Although the elastomeric behavior of the uncured SiB-1 copolymer decreased with time, curing stabilized the rubber by inhibiting crystallization.

### INTRODUCTION

The utilization of carboranesiloxane polymers (Fig. 1) as elastomers has been under intensive investigation for the last five years.<sup>1-3</sup> The first carborane to be evaluated for this application was *m*-carborane, i.e., 1,7-dicarba-*closo*-dodecarborane-12( $1,7-C_2B_{10}H_{12}$ ). This largest of the carboranes (number of boron atoms  $x = 10$ ) was incorporated into a silicone-like structure by preparing the bischlorodimethylsilyl and bismethoxydimethylsilyl derivatives and condensing the two in the presence of a ferric chloride catalyst to yield a hard crystalline SiB-1 polymer (Fig. 1a). However, to obtain elastomeric properties it was found necessary to copolymerize the bismethoxydimethylsilyl *m*-carborane monomer with either dichlorodimethylsilane to yield a SiB-2 polymer (Fig. 1b) or dichlorotetramethylidisiloxane to yield a SiB-3 polymer (Fig. 1c) (where 2 and 3 refer to the numbers of oxygen atoms separating the carborane units). Although the thermal stability of the elastomeric SiB-2 and SiB-3 polymers based on  $1,7-C_2B_{10}H_{12}$  was superior to that of unmodified methylsilicones, it was, nevertheless, inferior to that of the corresponding SiB-1 polymers. The lower thermal stability of the SiB-2 and SiB-3 relative to the SiB-1 polymers is presumed to be due to the —O—Si—O— bonds in the polymer backbone which in effect converts them from modified carborane into modified silicone polymers. The desirability of retaining the "short" siloxane moiety to maximize thermal stability while, if possible, also retaining the elastomeric property was suggested to one of our associates<sup>4</sup> several years ago.

Two years ago, synthetic routes to the lower carboranes ( $x < 10$  in Fig. 1) were developed to the point at which sufficient quantities became available

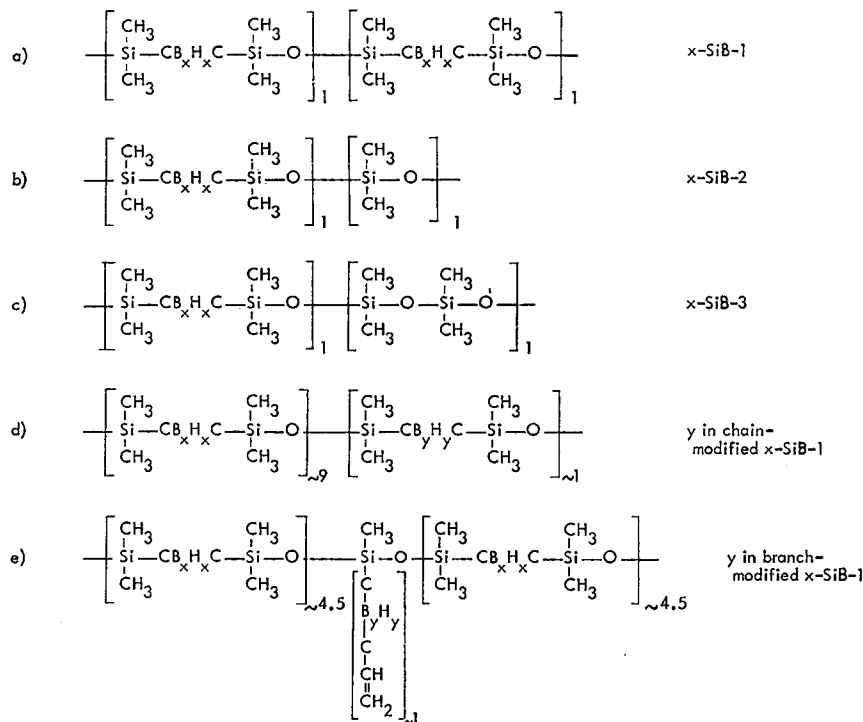


Fig. 1. Carboranesiloxane polymers.

for the inception of a polymerization program.<sup>5</sup> Such a program was deemed desirable for several reasons: The properties of the polymers from the smaller carboranes were unknown; the size of the smaller carboranes made their inclusion into an elastomeric backbone seem sterically favorable; and their small size suggested certain routes to the production of elastomeric SiB-1 polymers.

The present paper is the first in a series dealing with the preparation of carboranesiloxane polymers from the smaller carboranes. It is concerned with the synthesis and certain aspects of the microcrystalline structure of both unmodified  $\text{C}_2\text{B}_5\text{-SiB-1}$  polymers and of  $\text{C}_2\text{B}_5\text{-SiB-1}$  polymers whose crystallinity has been disrupted, and elastomeric behavior induced, by copolymerization with monomers containing the larger ( $\text{C}_2\text{B}_8$ , Fig. 1d, and  $\text{C}_2\text{B}_{10}$ , Fig. 1e) carborane moieties.

## EXPERIMENTAL

**2,4-Dicarb-*closo*-heptaborane-7 (I).** A mixture of the smaller, i.e.,  $\text{B}_3\text{-B}_5$ , *closo*-carborane prepared according to the procedure of Ditter and co-workers<sup>6</sup> was separated on a gas chromatograph (Hewlett Packard Model 776 equipped with four columns of 4 ft  $\times$  2.5 in. O.D. packed with Apiezon-L on Chromosorb-P). To  $\text{C}_2\text{B}_5\text{H}_7$  (>99% pure, containing <1%  $\text{B}_5\text{H}_9$ ) was

added sufficient anhydrous diethyl ether to make a 2.0*M* solution. Sodium hydride was then added in 100% excess to remove the last vestige of B<sub>5</sub>H<sub>9</sub>, and the solution was stirred for 2 hr before being vacuum transferred into a storage bulb.

**2,4-Dilithio-2,4-dicarba-closo-heptaborane-7 (II).** The entire preparation was carried out in a drybox. To 35.1 g (0.412 mole) of C<sub>2</sub>B<sub>5</sub>H<sub>5</sub> (2.0 *M*) in ether at  $-5 \pm 2^\circ\text{C}$  was added 120 ml of anhydrous hexane. *n*-Butyllithium, 1.2 moles (1.6*M* in hexane), was then added dropwise with stirring over a 2- to 3-hr period. The salt (II) was precipitated by the addition of 400 ml of hexane to yield 68.0 g of pale-yellow powder, the etherate of II.

**2,4-Bis(chlorodimethylsilyl)-2,4-dicarba-closo-heptaborane-7 (III).** To a three-necked 3-liter flask equipped with a stirrer, thermometer, nitrogen inlet, and addition funnel were added 520 ml of (CH<sub>3</sub>)<sub>2</sub>SiCl<sub>2</sub> (dist. 3 $\times$ ) and 1 liter of anhydrous ether. The addition funnel contained a slurry of 178 g of II etherate in 800 ml of hexane. Addition of the slurry occurred over a period of 2 hr while the flask was held at 0°C. The solution was filtered and distilled under vacuum through a 48-in.-column packed with glass helices; 110.35 g of III was collected at 64°–66°/0.9 mm (32.3% yield, based on C<sub>2</sub>B<sub>5</sub>H<sub>7</sub> starting material).

**2,4-Bis(methoxydimethylsilyl)-2,4-dicarba-closo-heptaborane-7 (VI).** To a 500-ml flask filled with a stirrer and attached to a vacuum line were added 100 g (0.369 mole) of III and 75 g (1.173 moles) of anhydrous methanol. After stirring at room temperature for 2.5 hr, methanol and HCl were evaporated, and the procedure was repeated to produce a quantitative yield of IV.

**The Poly-C<sub>2</sub>B<sub>5</sub>H<sub>5</sub>-Carboranylenesiloxane Analog of SiB-1 (V).** To a reactor containing 9.515 g (0.0351 mole) of III and 9.20 g (0.0351 mole) of IV was added 0.23 g (2 mole-% based upon total moles of III and IV) of anhydrous FeCl<sub>3</sub>.<sup>1-3</sup> After evacuation at room temperature the solution was slowly raised to 185°C. After a total reaction time of 3 hr, the solution was cooled and an additional 0.23 g of FeCl<sub>3</sub> was introduced. The reaction was continued at 185°C in vacuo until the evolution of methyl chloride was complete. The raw polymer was dissolved in hot xylene, filtered, precipitated with methanol, washed with aqueous acetone, redissolved in xylene, and reprecipitated with methanol to yield 14.8 g (97.7%) of V, a hard wax ( $\bar{M}_n = 12,500$ ).

**Dimethoxy(1-vinyl-*o*-carborane-2-yl)methylsilane (VI).** To 29.7 g (0.10 mole) of dichloro(1-vinyl-*o*-carborane-2-yl)methylsilane, prepared according to the procedure of Heying et al.,<sup>6</sup> was added an excess of methanol as in the synthesis of IV above. The procedure was repeated three times to yield VI, a white solid, in quantitative yield.

**1,10-Bis(methoxydimethylsilyl)-1,10-dicarba-closo-decaborane-10 (VII).** This compound prepared in the same manner as IV above but from 1,8-bis(chlorodimethylsilyl)-closo-1,10-dicarbadeccaborane-10 obtained through the courtesy of Professor F. Hawthorne and Mr. P. Garrett of UCLA. Future publications describing carboranesiloxane polymers in which the

$C_2B_8$  moiety is the principal component will be issued jointly with Professor Hawthorne and Mr. Garrett.

**$CH_2=CH(C_2B_{10}H_{11})$ -Modified Poly- $C_2B_5H_5$ -Carboranylenesiloxane Analogs of SiB-1 (VIII).** To 50 mole-% of III and to 45, 40, and 35 mole-% of IV were added 5, 10, and 15-mole-%, respectively, of VI and 2 mole-% of  $FeCl_3$ . The reaction was carried out as for V above.

**$C_2B_8H_9$ -Modified Poly- $C_2B_5H_5$ -carboranylenesiloxane Analogs of SiB-1 (IX).** To 50 mole-% of III and 45 and 40 mole-% of IV were added 5 and 10 mole-%, respectively, of VII and 2 mole-%  $FeCl_3$ . The reaction was carried out as for VIII above.

Differential scanning calorimetry (DSC) measurements were made on a du Pont Model 600 instrument at a scanning rate of  $15^\circ C/min$ . Infrared spectrograms of xylene-cast films were obtained on a Perkin Elmer Model 21 infrared spectrophotometer.

Samples of  $C_2B_5$ -SiB-1 modified with 10-mole-% (8.23 wt-%) of  $C_2B_8$  were compounded as follows: 100 parts resin; 10 parts  $SiO_2$  (Quso F-20, Philadelphia Quartz Company); and 5 parts  $Fe_2O_3$  (Mapico Red-297, Columbia Carbon Company). The mixture was blended on a hot two-roller mill and divided into two portions, to one of which was added 0.5 part of 2,4-dichlorobenzoyl peroxide (K and K Laboratories). The sample containing the peroxide was cured at  $260^\circ C$  for 26 hr. The rate of crystallization for both elastomers was estimated by measuring sample hardness (Shore A scale) with a durometer (PTC Instruments).

## RESULTS AND DISCUSSION

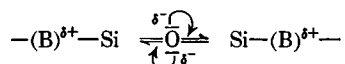
### Synthesis

The preparation of II (repeated over 20 times during the past two years) proceeded readily at  $-5^\circ C$ , in contrast to the recent experience of Grimes<sup>7</sup> who prepared II at the higher temperature of  $25^\circ C$ . Unlike the dilithio salt of *m*-carborane ( $x = 10$ ), II was only slightly soluble in ether. It did, however, form an etherate which could be obtained in the form of a dry powder by the addition of hexane. Compound II was added to dimethyldichlorosilane as a slurry in hexane in order to form III.<sup>8</sup> The reverse addition was not considered desirable because various secondary reactions could occur unless dimethyldichlorosilane was at all times present in excess. Although III was initially purified on a gas chromatograph, a product of equivalent purity was subsequently obtained by vacuum distillation. The conversion of III to IV proceeded uneventfully. The polymerization reactions proceeded smoothly but not rapidly. This may have been due to steric hindrance and/or competition between condensation and substitution reactions. The fact that all of the SiB-1 polymers prepared were completely soluble in hot xylene indicated that only a minimal amount, if any, of undesired crosslinking reactions occurred.

## Characteristics of SiB-1 Carboranesiloxane Polymers

### *Thermal Stability*

The substantial thermal stability of the polydimethyl- and polydiphenylsiloxanes can be attributed to the stability of the Si—O—Si bond. However, thermal depolymerization by catalyst residues introduced during polymer preparation, by metal compounds which act as Lewis acids, and by water vapor, does occur. The incorporation of electron-deficient moieties such as the carboranes (B)<sup>δ+</sup> tends to oppose depolymerization by strengthening the siloxane bond via increasing  $d\pi-p\pi$  bond contributions:<sup>9</sup>



Because the extent of this bond-strengthening inductive effect will be proportional to the concentration of carborane in the polymer, SiB-2 and SiB-3 varieties exhibit lower thermal stability than SiB-1 types.

### *Crystalline versus Elastomeric Behavior*

Two principal factors contribute to elastomeric behavior: (1) a coiled molecular configuration which can be uncoiled by the application of suitable stresses; and (2) low cohesive energy between segments on the same or different polymer chains, i.e., weak intra- and intermolecular forces.

The cohesive energy in the polydimethylsiloxane elastomers is of an extremely low order,<sup>10</sup> a condition which is attributable to a fairly homogeneous distribution of electrons along the entire molecule. However, the introduction of electropositive (carborane) sites along a polymer segment increases the latter's affinity for electronegative (oxygen) sites along another polymer segment, so that the cohesive energy density of the carboranesiloxanes is higher than that of the unmodified siloxanes. Higher cohesive energy, then, results in an increased tendency to crystallize, a situation which is exacerbated when steric regularity also tends to favor crystallinity. It is apparent that steric regularity is at a maximum in the SiB-1 carboranesiloxanes (Fig. 1a) and decreases with increasing concentration of —Si—(CH<sub>3</sub>)<sub>2</sub>—O— groups. Thus the elastomeric behavior of the SiB-2 (Fig. 1b) and SiB-3 (Fig. 1c) polymers is superior to that of SiB-1 polymers for both steric and electrostatic reasons. In the case of the C<sub>2</sub>B<sub>10</sub> carboranesiloxanes, a compromise was eventually reached between thermal stability on the one hand and acceptable elastomeric behavior on the other by the development of the SiB-2 and, more recently, the SiB-3 polymers. Further developmental work on the polymer with the highest thermal stability, C<sub>2</sub>B<sub>10</sub>-SiB-1, has apparently been abandoned because of its high crystallinity and consequent poor elastomeric properties.

The availability of the smaller carboranes appeared to offer a solution or at least an alternative to this dilemma for two reasons: (1) the presence of the smaller units enhanced the possibility of achieving the tightly coiled

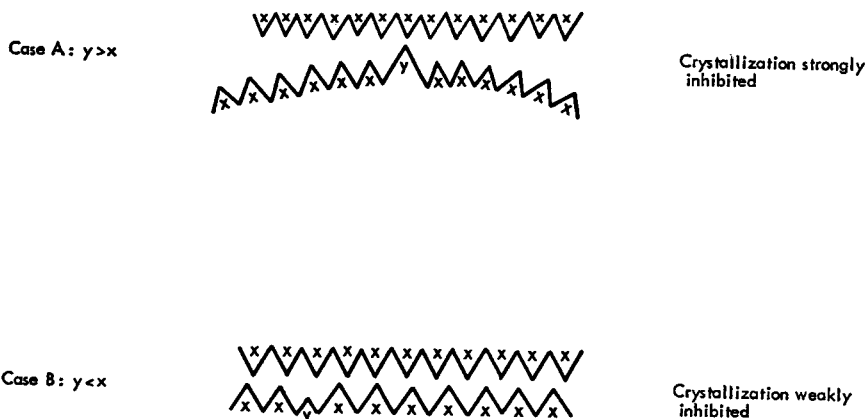


Fig. 2. Schematic representation of crystallite disruption in  $x$ -SiB-1 carboranesiloxane polymers by the inclusion of an occasional  $y$ -carborane where (A)  $y > x$ ; (B)  $y < x$ .

configuration characteristic of elastomers; (2) the structural regularity, and hence tendency to crystallize, of smaller units is more easily disrupted by the insertion of an occasional large moiety than vice versa (Fig. 2).

The lesser bulk of the smaller carboranes was not sufficient per se to induce elastomeric behavior into a  $C_2B_5$ -SiB-1 polymer, and the product obtained was a hard wax whose Si—O—Si band was characterized by an infrared doublet with maxima at 9.05 and 9.45 microns (Fig. 3a). This spectral feature was similar to that observed for the  $C_2B_{10}$ -SiB-1<sup>11</sup> but was unlike the singlet observed for  $C_2B_5$ -SiB-2.<sup>12</sup> This suggested that the SiB-1 doublet may be the result of restricted mobility of the Si—O—Si bond owing to electrostatic interactions between the carborane moieties and oxygen atoms in contiguous segments which resulted in crystallite formation.

TABLE I  
DSC Study of the Disruption of  $(C_2H_5)_2$ -SiB-1 Crystallinity by the  
Inclusion of  $C_2B_8$  and  $C_2H_{10}$  Comonomers

Comono- mer	Comonomer content		Crystallinity index $A_N^a$	Melting temp, $T_m$ , °C	Glass temp $T_g$ , °C
	mol-%	wt-%			
None	0	0	1.0	70	4 <sup>b</sup>
$C_2B_8$	5	5.50	0.795	54	-27 <sup>b</sup>
$C_2B_8$	10	8.28	0.0535	58, 45	-50
$C_2B_{10}$	5	5.28	0.0437	59	-59
$C_2B_{10}$	10	10.23	0.01995	60.5	-54
$C_2B_{10}$	15	15.83	0.00536	61	-52

<sup>a</sup>  $A_N$  = Area under DSC curves for samples of equal weight, normalized with respect to the unmodified  $C_2B_5$ -SiB-1.

<sup>b</sup> These values are not well defined (see Figs. 4 and 5).

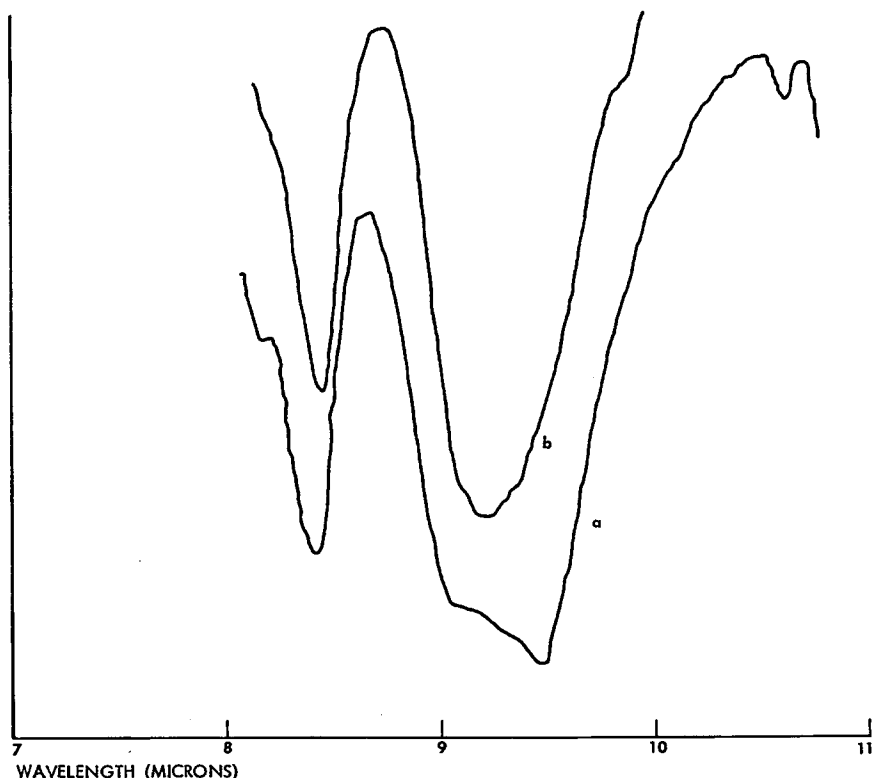


Fig. 3. Infrared, spectra of  $C_2B_5$ -SiB-1's samples (a) and (b) containing 0 and 5 mol-%  $C_2B_5$ , respectively.

At this juncture it was decided to determine whether the introduction of occasional larger carborane moieties would disrupt crystallinity sufficiently so as to result in an elastomeric SiB—1. The feasibility of this approach was suggested by previous work which showed that the stiffening temperature (a measure of crystallization tendency) of polydimethylsiloxanes was decreased from  $-40^\circ\text{C}$  to a minimum of  $-112^\circ\text{C}$  by the introduction of 7.5 mol-% of phenyl groups.<sup>12</sup> This study also suggested the molar concentration range over which any such effect might manifest itself most strongly, viz., between 5 and 15 mole-%. Toward this end two series of polymers were fabricated: (1) that in which the comonomer was VI; and (2) that in which the comonomer was VII.

Fortunately, the introduction of between 5 and 15 mole-% of VI or VII did indeed have the desired effect of disrupting crystallinity (Table I, Figs. 4 and 5). The raw polymers were highly elastomeric and soluble in hot xylene (no crosslinking). The Si—O—Si band of a  $C_2B_5$ -SiB-1 containing 5 mole-% of  $C_2B_5$  was a singlet (Fig. 3b). This is believed to be indicative of less restricted motion and hence more amorphous character than the unmodified SiB—1. The DSC study yielded qualitative, and even quan-

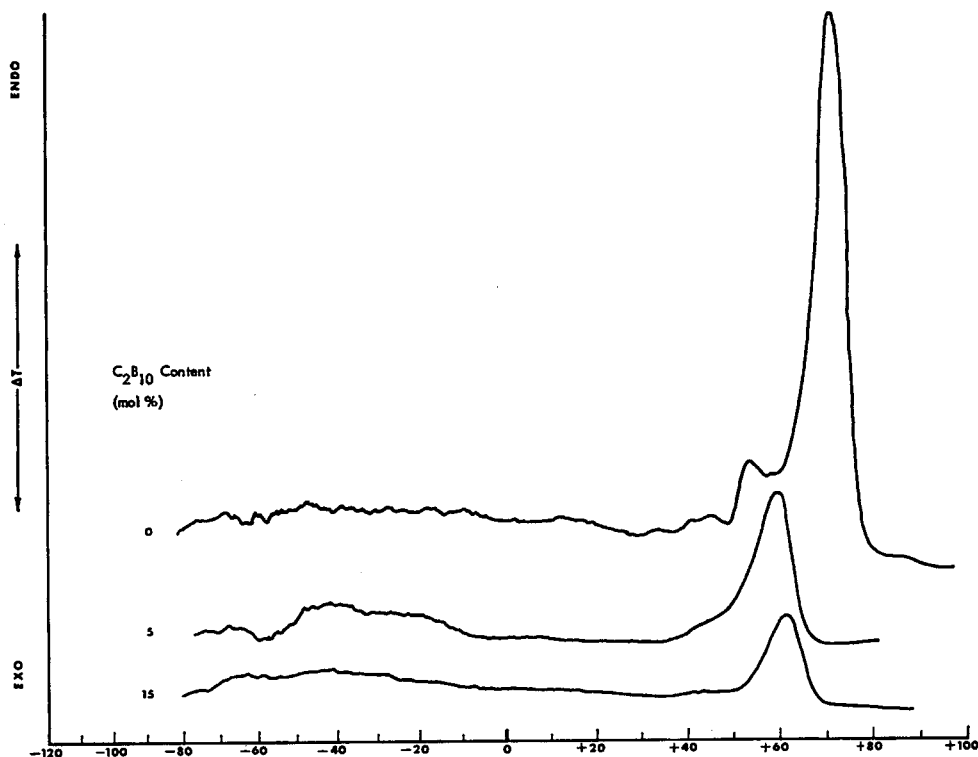


Figure 4. DSC tracings for  $C_2B_6$ -modified  $C_2B_6$ -SiB-1 elastomers.

titative, information as to the extent of crystallite disruption by the insertion of an occasional large carborane unit (Table I, Figs. 4 and 5). A crystallinity index  $A_N$  was defined for which the sample exhibiting the highest extent of crystallinity, viz., the unmodified SiB-1, was arbitrarily assigned a value 1.0. The area under the DSC curves of the various samples was then integrated and normalized relative to the unmodified SiB-1 after making suitable corrections for minor variations in sample size. Figures 4 and 5 are representative of the raw DSC (uncorrected for sample size) tracings.

Several important characteristics are apparent:

1. The complexity of the unmodified is much greater than that of the modified SiB-1 polymers. Five separate DSC peaks, two of which are most prominent, are discernible in the case of the former, whereas the latter are characterized by at most two separate melting domains. These domains are believed to correspond to variations in crystallite size and/or order. (Small and/or less perfect crystallites melt at lower temperatures than large and/or more ordered structures.)

2.  $A_N$  decreases with increasing concentration of the order-disrupting larger carboranes. This fact constitutes strong evidence for the validity of



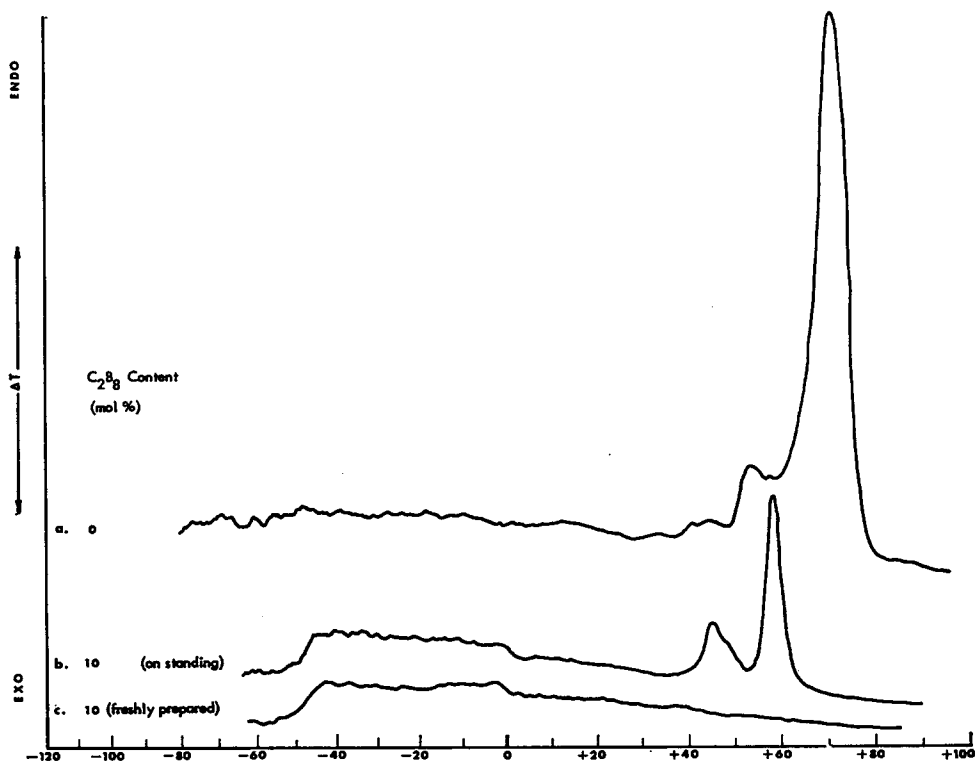


Fig. 5. DSC tracings for  $C_2B_{10}$ -modified  $C_2B_5$ -SiB-1 elastomers.

the assumption that the presence of occasional large units can successfully disrupt crystallinity.

3. The values of  $T_m$  and  $T_g$  decrease with increasing concentration of  $C_2B_8$  (Fig. 4 and Table I). However, the  $T_g$  values for the unmodified SiB-1 and the sample containing 5 mole-% of  $C_2B_8$  are at best barely discernible and may, therefore, be erroneous. Decreasing values of  $T_m$  and  $T_g$  are further indications of decreasing crystallite size and/or structural order.

4. The values of  $T_m$  and  $T_g$  increase slightly with increasing concentration of the vinyl- $C_2B_{10}$  moiety (Fig. 5, Table I). This somewhat unexpected result is not indicative of increased crystallinity ( $A_N$  decreases even more dramatically than for equivalent  $C_2B_8$  incorporation), but instead is indicative of the presence of the vinyl groups, a fraction of which have very probably participated in crosslinking the polymer. An increase in  $T_m$  and  $T_g$  with increasing crosslink density is not unusual because of the inhibiting effect of crosslinking upon segmental mobility.

The  $C_2B_8$ - and vinyl- $C_2B_{10}$ -modified  $C_2B_5$ -SiB-1 polymers are, of course, not strictly comparable. The  $C_2B_8$ -modified polymers are true SiB-1 polymers in every respect because the 1,10- $C_2B_8$ -carborane is incorpo-

rated into the polymer backbone in the usual manner (Fig. 1d), while the vinyl- $C_2B_{10}$ -1 polymers, on the other hand, are not only found on side branches but also contain the vinyl grouping (Fig. 1e). These effects account for most of the more efficient crystallinity disruption of the  $C_2B_{10}$  modifier. Five mole-% of vinyl- $C_2B_{10}$  reduces the crystallinity to approximately one twentieth of the unmodified  $C_2B_5$ -SiB-1, a decrease which requires 10 mole-% of the  $C_2B_8$  to equal (Table I). Had both polymers of the "y in chain" type (Fig. 1d), a much smaller difference between the two would have been expected. Nevertheless, even in such a case the  $C_2B_{10}$  modifier should be slightly more efficient than the  $C_2B_8$ , both because of the greater size of the former and because the carbon atoms are in the ortho position in  $C_2B_{10}$  and in the para position in  $C_2B_8$ . The para position possesses greater structural regularity than the ortho position and consequently may be expected to exert a somewhat lesser order-disrupting influence.

The modified SiB-1 polymers are highly elastomeric materials when freshly prepared, and their DSC tracings are indicative of a complete absence of crystallinity (Fig. 4c). On standing, however, crystallization does occur (Fig. 4b), and decreasing elasticity and increasing hardness with time are clearly apparent. This tendency to crystallize with time is attributable to the persistence of the previously mentioned electrostatic interactions that occur in spite of steric hindrance to the formation of virtual crosslinks. It was felt, however, that the introduction of covalent crosslinks into the polymer might provide a practical means for inhibiting the inter- and intramolecular realignment which ultimately results in crystallization.

The experiment which was devised to test this hypothesis involved the use of a peroxide catalyst in the test sample to effect crosslinking and unequivocally demonstrated the feasibility of this approach (Fig. 6).

Two blanks were employed: a highly crystalline unmodified SiB-1 and one containing 10 mole-% of  $C_2B_8$  in chain. The rate of crystallization was conveniently followed by measuring the shore A hardness (the most convenient measure of crystallinity available) versus time at  $23^\circ \pm 1^\circ C$ . The most important results of this study are: (1) crystallization can be inhibited by crosslinking; (2) the hardness of the cured specimen increased very slightly over the course of 16 hr and not at all thereafter; (3) the hardness of the uncured specimen, on the other hand, increased very rapidly and exceeded that of the cured specimen after 5 hr; and (4) the hardness of the uncured sample continued to increase over the course of several days, asymptotically approaching a value at infinite time somewhat below that of the unmodified SiB-1.

In summary, the feasibility both of *producing* elastomeric  $C_2B_5$ -SiB-1 polymers by the disruption of crystallization by the inclusion of occasional larger carborane moieties and of *maintaining* the elastomeric behavior so induced by the introduction of covalent crosslinks has been demonstrated. Additional work is, however, necessary to determine the thermal stability of the polymers so produced and to increase molecular weight and to deter-

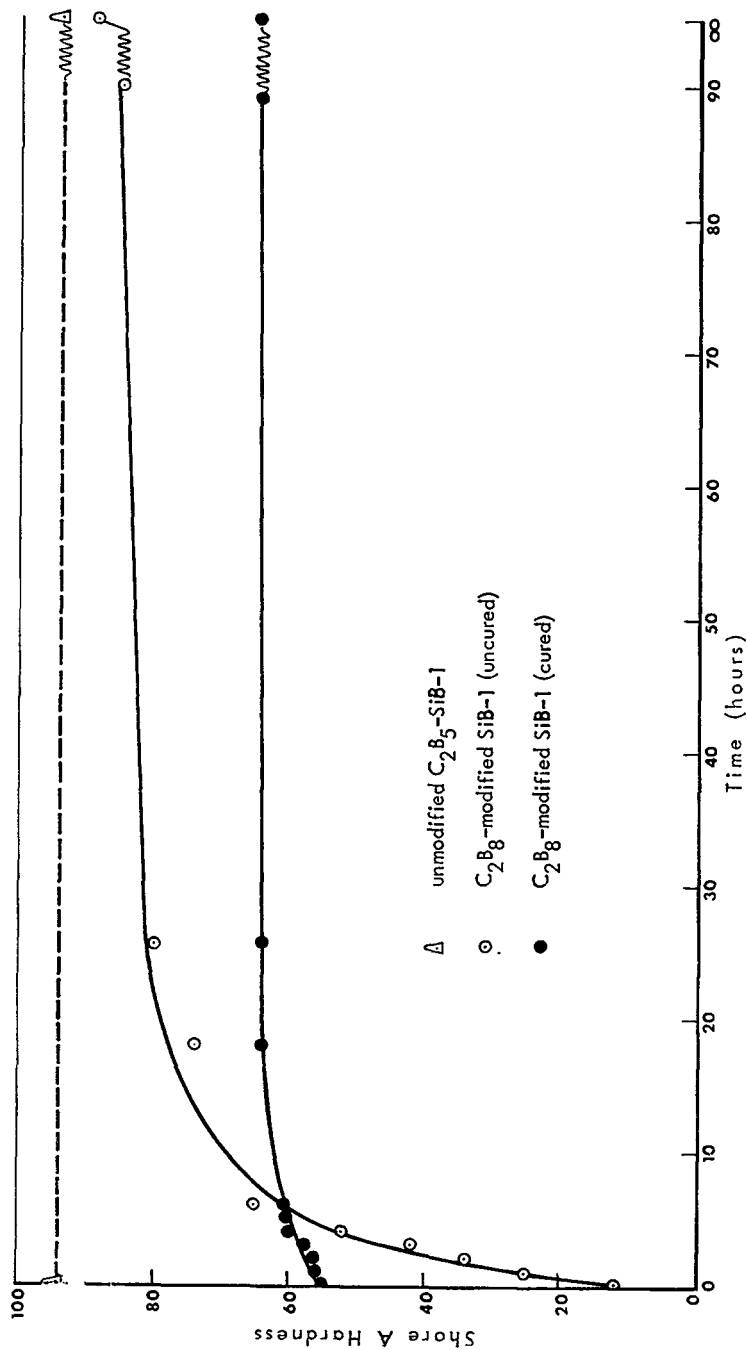


Fig. 6. Shore A hardness versus time for  $C_2B_8$ -SiB-1 carboranesiloxane polymers: ( $\Delta$ ) unmodified  $C_2B_8$ -SiB-1; ( $\circ$ )  $C_2B_8$ -modified SiB-1 (uncured); ( $\bullet$ )  $C_2B_8$ -modified SiB-1 (cured).

mine optimum modifier concentrations, compounding formulations, and curing conditions.

A subsequent report on the  $C_2B_5$  analogs of the  $C_2B_{10}$ -SiB-2 polymers is currently in preparation. A report on the  $C_2B_8$  analogs of the  $C_2B_{10}$ -SiB-2 polymers will also be issued in the near future in collaboration with Professor M. F. Hawthorne and Mr. P. M. Garrett of UCLA.

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### References

1. S. Papetti, B. Schaeffer, A. Gray, and T. Heying, *J. Polym. Sci. A-1*, **14**, 1623 (1966).
2. H. Schroeder, O. Schaffing, T. Larcher, F. Frulla, and T. Heying, *Rubber Chem. Tech.*, **39**, 1184 (1966).
3. H. Schroeder, *Rubber Age*, **101**, 58 (1969).
4. H. Fox, Personal Communication to R. E. Williams.
5. J. Ditter, J. Oakes, E. Klusmann, and R. Williams, *J. Inorg. Chem.*, **9**, 889 (1970).
6. T. Heying et al., *Inorg. Chem.*, **2**, 1089 (1963).
7. R. Grimes, Paper Presented at ONR Boron Conference, Stamford, Conn., Sept. 1969.
8. M. F. Hawthorne, Personal Communication.
9. W. Noll, *Chemistry and Technology of Silicones*, Academic Press, New York, 1968.
10. F. Billmeyer, *Textbook of Polymer Science*, Wiley, New York, 1965.
11. R. E. Williams and R. E. Kesting, Paper Presented at ONR Boron Conference, Stamford, Conn., Sept 1969.
12. K. Polmanteer and M. Hunter, *J. Appl. Polym. Sci.*, **1**, 3 (1959).

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