

Heat-Resistant Polymers Containing the Low Molecular Weight *Closo*-Carboranes. II. Thermal Behavior of Polycarboranesiloxane SiB-1 Elastomers from $C_2B_5H_7$

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Synopsis

Unmodified 5-SiB-1 polymers have been found to be virtually equivalent to their 10-SiB-1 counterparts with respect to thermal stability. The 5-SiB-1 polymers, however, are substantially more amenable to conversion into elastomers. The introduction of 15 to 20 mole-% of *m*- C_2B_{10} into the 5-SiB-1 backbone results in elastomers whose thermal stability, although less than that of the parent homopolymer, is nevertheless substantially in excess of the published values for the higher SiB polymers. The crystallization of the 5-SiB-1 copolymer containing 15 mole-% C_2B_{10} was inhibited by irradiation with 50 megarads of 3 MeV betas. The 5-SiB-1 copolymer containing 20 mole-% C_2B_{10} , on the other hand, remained a rubber at room temperature.

INTRODUCTION

The production of elastomers of the *x*-SiB-1 type, $(-SiR_2CB_xH_xCSiR_2-O)_n$, (where *x* refers to the number of boron atoms in the carborane and 1 to the number of oxygen atoms separating the monomer units) has long been deemed desirable because this class of polycarboranesiloxane is not subject to the redistribution reactions which occur in the presence of the $-O-SiR_2-O-$ moieties found in the higher SiB polymers and because it contains the maximum concentration of carborane, the moiety which is primarily responsible for the thermal stability of the polymer.¹⁻³ Although pure SiB-1 species are highly crystalline, elastomeric behavior has recently been induced into a SiB-1 polymer of the small *closo*-carborane, $C_2B_5H_7$, by the disruption of the crystal lattice of the homopolymer via the inclusion of small amounts of comonomers containing the larger carboranes $C_2B_8H_8$ and $C_2B_{10}H_{10}$.^{4,5} In this paper the thermal behavior of the 5-SiB-1 elastomers containing small amounts of meta $C_2B_{10}H_{10}$ is considered.

EXPERIMENTAL

Polymer Synthesis

The 5-SiB-1 elastomers were prepared according to the procedure described earlier.^{4,5} The $C_2B_{10}H_{10}$ moiety was added as the methoxy mo-

nomer (1,7-bis(methoxydimethylsilyl)-*m*-carborane) to replace an equimolar aliquot of the corresponding methoxy monomer of $C_2B_5H_7$, $CH_3OSi(CH_3)_2-CB_5H_5CSi(CH_3)_2OCH_3$. Two mole-% (based on the total moles of monomers) of anhydrous $FeCl_3$ and 7 mole-% of hydrated $FeCl_3$ were added to catalyze the condensations. The temperature was slowly raised to 185°C under a high vacuum. For purposes of comparison, the corresponding 10-SiB-1 polymer was also prepared according to a previously described procedure.⁶

Analysis

Number-average molecular weights \bar{M}_n were determined in xylene utilizing a vapor pressure osmometer (Mechrolab Model 301A). They are accurate to $\pm 10\%$. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were made on a du Pont Model 600 instrument. DSC scanning was at the rate of 15°C/min. TGA was in air at 1°C/min for the initial samples and at 5°C/min for subsequent samples after the equivalence of the two scanning rates had been established.

Curing

Samples of 5-SiB-1 elastomer containing 15 mole-% of C_2B_{10} comonomer were milled into sheets and then subjected to radiation dosages of from 0 to 50 megarads with 3 MeV betas from a linear accelerator. The effectiveness of the cure at inhibiting the hardening brought about by crystallization was estimated by measuring sample hardness (Shore A scale) with a durometer (PTC Instruments) as a function of postirradiation time.

EXPERIMENTAL RESULTS AND DISCUSSION

Synthesis

As described earlier,^{4,5} the polymerization reactions proceeded smoothly but not rapidly. The fact that both the rate of polymerization and catalyst solubility increased with increasing C_2B_{10} concentration indicated that the reaction may have been inhibited by a low effective catalyst concentration. More compatible catalysts are currently being investigated.

Comparison between 5-SiB-1 and 10-SiB-1 Homopolymers

A comparison between the properties of the 5-SiB-1 and 10-SiB-1 homopolymers is of importance both for its own sake and because of the fact that the two SiB-1 polymers, incorporating as they do the maximum concentration of carborane in the entire series of polycarboranesiloxane polymers, represent prototypes for a general comparison between the two carboranes.

The 5-SiB-1 homopolymer was a hard wax which was readily soluble in xylene. The 10-SiB-1 homopolymer was an extremely brittle solid which crumbled to a powder. Its solubility in cold xylene was insufficient to

permit a determination of its molecular weight but it did dissolve in hot xylene. Although the molecular weights of the two SiB-1 homopolymers differ to an unknown extent, differences in their physical properties are believed to be primarily due to the greater flexibility of the 5-SiB-1 polymer molecules. The lower T_g and T_m values of the 5-SiB-1 are likewise attributable to the lesser interference with rotation of the Si—O—Si bond by the smaller carborane. Chain flexibility is, of course, of paramount importance since elastomeric behavior is the objective. Apparently the 10-SiB-1 is considerably more crystalline and remains so to a higher temperature than the 5-SiB-1 variety.

These findings were not unexpected, and indeed the superior physical properties of the 5-SiB-1 polymer had been correctly predicted from a priori considerations. Unpredictable, however, was the fact that the 5-SiB-1 exhibited comparable thermal stability to its 10-SiB-1 counterpart (Table I). It should be kept in mind that the 5-SiB-1 and 10-SiB-1 polymers compared in this study were prepared under comparable experimental conditions in the same laboratory. It may be that the electron deficiency of the C_2B_5 moiety is sufficient to stabilize the Si—O—Si bond against thermal degradation to the maximum extent permissible in a polycarboranesiloxane polymer. If this is the case, then any possibly greater electron deficiency inherent in the $C_2B_{10}H_{10}$ moiety relative to that of the $C_2B_5H_7$ moiety would simply not be utilizable in the polycarboranesiloxanes. In summary, it appears that 5-SiB-1 and 10-SiB-1 polymers are comparable with respect to thermal stability, but that polymers of the smaller species are inherently more suitable for incorporation into elastomeric materials.

TABLE I
A Comparison Between the Solubility and Physical and Thermal Properties of the 5-SiB-1 and 10-SiB-1 Homopolymers

| Polymer | \bar{M}_n | Solubility | Hardness and brittleness | T_g , °C | T_m^a , °C | Weight loss in air, % | |
|----------|-------------|----------------|--------------------------|-------------------|-----------------------|-----------------------|----------|
| | | | | | | at 450°C | at 900°C |
| 5-SiB-1 | 12,500 | decreasing | increasing | -62 | 73 | 0.0 | 7.0 |
| 10-SiB-1 | insoluble | ↓ | ↓ | (25) ^b | 238(240) ^b | 2.3(0.0) ^c | 9.1 |

^a Crystalline melting point.

^b Value obtained from stress relaxation measurements.⁷

^c Previously reported value.²

5-SiB-1 Polymers Containing Small Amounts of m - C_2B_{10} as a Comonomer

In an earlier study, the feasibility of converting the highly crystalline 5-SiB-1 homopolymer into an amorphous and elastomeric 5-SiB-1 copolymer by the introduction of small amounts of vinyl *ortho*- $C_2B_{10}H_{10}$ - or $C_2B_8H_8$ -containing monomers was demonstrated.^{4,5} The incorporation of

between 5 and 15 mole-% of the larger carboranes as comonomers reduced the crystallinity of the 5-SiB-1 polymer by two orders of magnitude with corresponding dramatic improvements in the elastomeric behavior of the resultant polymers. In this study, the effects of the incorporation of between 5 and 20 mole-% of the m -C₂B₁₀ into the backbone of the 5-SiB-1 polymer have been investigated (Table II).

TABLE II
Elastomeric Character, Transition Temperatures, and Weight Loss of 5-SiB-1 Polymers Containing Small Amounts of m -C₂B₁₀ in Chain

| C ₂ B ₁₀ , mole-% | \bar{M}_n | Elastomeric character | T_g , °C | T_m , °C | Weight loss in air at 450°C, % |
|--|-------------|--------------------------|------------------|---------------------|--|
| 0 | 12,500 | ↑ increasing ↓ | -62 | 73, 70 ^b | 0 |
| 5 | 2,580 | | — | 57 | 1 |
| 10 | 2,920 | | -53 ^a | 56 | 2 |
| 15 | 3,170 | | -45 ^a | 52 | 4 |
| 20 | 3,830 | | — | ^c | 4 |

^a Approximate values, i.e., unequivocal values were not obtainable from DSC tracings.

^b Previously reported value.^{4,5}

^c No P_m , i.e., polymer appears to be completely amorphous.

Molecular weight increases with the increasing concentration of m -C₂B₁₀ monomer in the copolymers, owing to increasing homogeneity in the polymerization reaction. With increasing comonomer concentration, the 5-SiB-1 polymers also become markedly less crystalline and their elastomeric character more pronounced. As an additional indication of decreased crystallinity, T_m values experience substantial decreases (Table II). It may be significant that the 5-SiB-1 polymer containing 20 mole-% of m -C₂B₁₀ does not appear to possess a well defined T_m . This polymer also retains its elastomeric behavior, whereas those copolymers in this series which do exhibit a T_m harden slowly upon standing.

Although the thermal stability of the 5-SiB-1 polymers experiences a modest decrease with increasing comonomer concentration and thus increasing elastomeric behavior, it nevertheless remains higher than SiB-2 or SiB-3 polymers prepared by ourselves and others. This decline in thermal stability with increasing C₂B₁₀H₁₀ content may be related to increasing accessibility to oxygen with decreasing crystallinity. Because it retains its elastomeric behavior upon prolonged standing, the 5-SiB-1 polymer containing 20 mole-% of the m -C₂B₁₀ carborane represents an excellent candidate for development into a practical high-temperature rubber. Work is in progress to increase the molecular weights of this species so as to further enhance its elasticity and increase its strength.

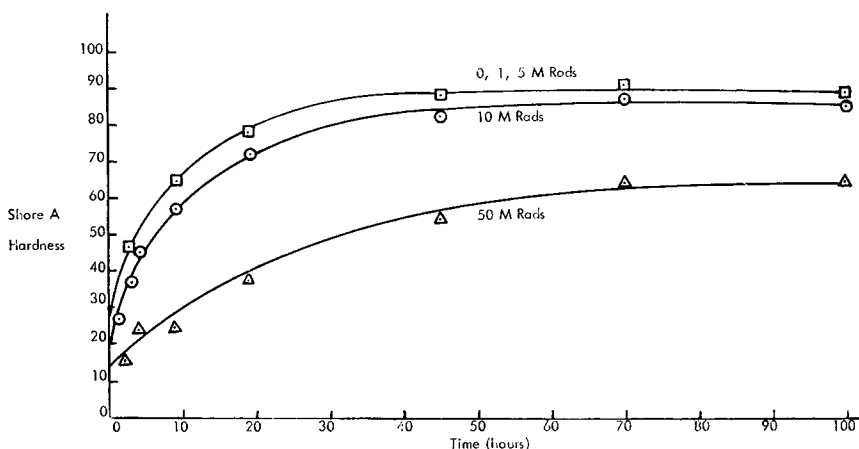


Fig. 1. Shore A hardness vs. time and β -irradiation dose (3 MeV) for a 5-SiB-1 containing 15 mole-% m -C₂B₁₀.

Irradiation Curing of 5-SiB-1 Polymers Containing 15 Mole-% C₂B₁₀

In an earlier study,^{4,5} the inhibition of crystallization (and hence the maintenance of elastomeric behavior) in 5-SiB-1 elastomers by peroxide curing was considered. It is also possible to inhibit crystallization by high-energy irradiation-induced crosslinking. However, the doses necessary to effectively crosslink the 5-SiB-1 elastomers appear to be higher than the 10 megarads normally required for curing the polydimethylsiloxanes.⁸ No difference was detectable in the rate of crystallization (as estimated by measurements of hardening) for doses below 10 megarads, where a slight effect was noticed (Fig. 1). At 50 megarads, however, a substantial effect was in evidence. It is perhaps more than coincidental that the end values (~ 60 on the Shore A scale) for both peroxide and β -irradiation curing were identical. It is conceivable that this value represents a minimum hardness value because of the combined effects of crosslinking and residual crystallization.

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