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Joseph Green[a]; Nathan Mayes[a]
[a] THIOKOL CHEMICAL CORPORATION, REACTION MOTORS DIVISION, DENVILLE, NEW JERSEY

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Thermal Stability of Carborane-Containing Polymers

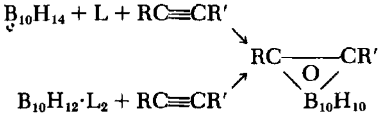
JOSEPH GREEN and NATHAN MAYES
THIOKOL CHEMICAL CORPORATION,
REACTION MOTORS DIVISION, DENVILLE, NEW JERSEY

Synopsis

Siloxane and benzimidazole polymers containing carborane groups were synthesized and their thermal stability was measured. The data show the stabilizing effect of the carborane group on the thermal and oxidative stability of the polymer. In many instances the increase in thermal stability has been attributed to the inductive effect of the carborane group. In one case the oxidative stability of a silicone polymer has been increased by a carborane group adjacent to the silicon atom carrying the methyl groups. Carborane in the backbone of a silicone polymer appears to have inhibited rearrangement to cyclic compound. Metal panels coated with carborane polymers appear to have outstanding stability, apparently due to the formation of a protective film during the heating cycle.

INTRODUCTION

The preparation of inorganic boron polymers has been extensively studied and reported in the literature (*1*–*3*). In the past few years covalent boron hydride polymers containing carborane in the polymer have been prepared. *o*-Carborane monomers are generally prepared by allowing acetylenic compounds to react with decaborane–Lewis base (L) mixtures of $B_{10}H_{12}\cdot L_2$ compounds (*4*,*5*), as shown below (*6*):



$$B_{10}H_{14} + L + RC\equiv CR' \rightarrow RC\overset{\quad}{-\!-}CR' \;(B_{10}H_{10}) \leftarrow B_{10}H_{12}\cdot L_2 + RC\equiv CR'$$

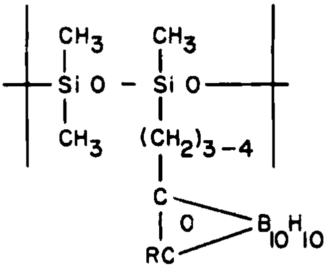
Carborane exists in three isomeric forms known as *ortho, meta,* and *para* carboranes, where the carbon atoms are (1, 2), (1, 7), and (1, 12) in the carborane basket or ring structure. The meta isomer has been formed by thermal rearrangement of *ortho*-carborane at a temperature of about 450°C and the *para* isomer has been formed by heating the *meta* isomer at about 600°C. Calculations of the size of the carborane nucleus, based upon a model for the proposed structure (*7*), show that it approximates a sphere with an effective van der Waals radius of 4 A. The *ortho*-carborane group is highly electrophilic; 1-methyl-2-carboranylcarboxylic acid has a pK_a value of 2.74 (*7*). The *meta* isomer is less electrophilic, the corresponding acid having a pK_a value of 3.14.

Various *o*-carborane monomers have been prepared, and these have been used for preparing polyesters (*8*), polyformals (*9*), polyacrylates (*10*), polysiloxanes (*11,12*), and polybenzimidazoles (*13,14*). Polysiloxanes and polybenzimidazoles have also been prepared with the *meta* isomer. Each of the polymers exhibits a thermal stability, as measured by TGA, which is greater than the corresponding noncarborane polymer. Of particular interest are the siloxane and benzimidazole polymers, which have been reported to possess greatly enhanced thermal stability. The subject of this paper is the thermal stability of polycarboranylsiloxanes and polycarboranylbenzimidazoles.

RESULTS

Carborane Siloxane Polymers

Two types of carborane siloxane polymer have been prepared: those containing *ortho*-carborane groups pendent to the siloxane chain and those containing *meta*-carborane groups in the polymer



where R = H, CH_3

backbone. Copolymers of dimethylsilane and methyl *o*-carboranylalkyl silanes exhibit thermal stabilities up to 450°C as measured by TGA (Figs. 1 and 2). The small weight loss occurring at about 300 to 325°C can be eliminated by heating the sample to 400°C in the TGA apparatus, cooling, and rerunning the TGA. No obvious change of the material has been noted during this prior treatment

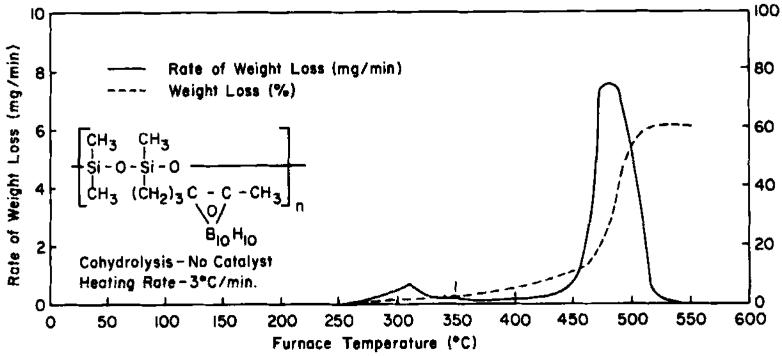


FIG. 1. Thermal gravimetric analysis of polycarboranylsilicone in N_2.

of the sample when it is conducted in an inert atmosphere. Thermal-oxidation temperatures for these polymers, however, are of about the same order of magnitude as for conventional organic polysiloxanes *(11)*.

The stability of these materials was determined also by the measurement of polymer molecular weight changes that occur on heating. The above polymer, which was apparently stable to about

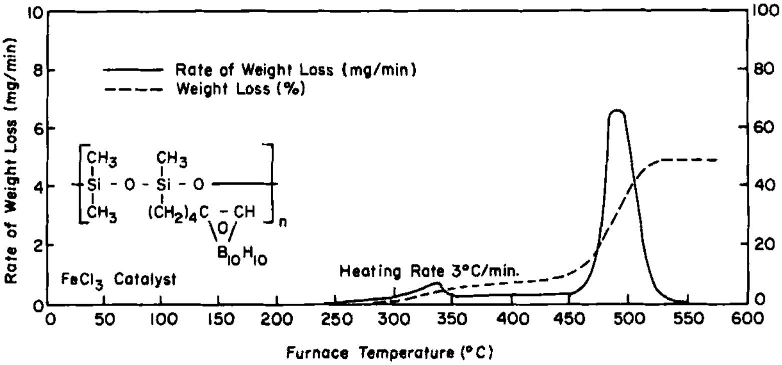
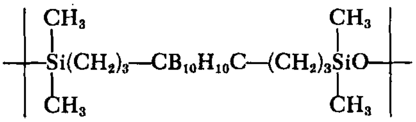


FIG. 2. Thermal gravimetric analysis of polycarboranylsilicone in N_2.

450°C by TGA, has been shown to undergo competing processes of polymerization and depolymerization on heating. The starting polymer, which has hydroxy terminals, continues to polymerize at high temperatures, but it also depolymerizes through cyclic formation, as does polydimethylsiloxane. Heating the polymer for 24 hr at 300°C resulted in a net change in molecular weight from 7700 to 4600.

Coatings of the above polymer have been applied to aluminum, stainless steel, and titanium panels, and cured to continuous films (*15*). These clear films have protected the substrates for 25 hr at 425 to 540°C in air; a glossy film appeared to protect the polymer. Aluminized films of the *o*-carborane silicone polymer on titanium have lasted 25 hr at 650°C with some discoloration. Titanium-dioxide–pigmented films have lasted 25 hr at 425 to 480°C on stainless steel.

m-Carboranylsiloxane polymers with the *m*-carborane group in the polymer backbone, as shown below, have been prepared (*12*). The methylene chains were incorporated into the polymer chain to obtain elastomeric materials. These polymers may be obtained



$$-\!\left[\overset{CH_3}{\underset{CH_3}{\mathrm{Si}}}(CH_2)_3-CB_{10}H_{10}C-(CH_2)_3\overset{CH_3}{\underset{CH_3}{\mathrm{Si}}}O-\right]\!-$$

as low-molecular-weight, soluble, somewhat elastic materials by hydrolysis-condensation polymerization of difunctional silane monomers or as apparently higher-molecular-weight, hardly soluble, elastic materials (tough elastomer) by ring-opening polymerization of a suitable carborane-siloxane cyclic compound. This polymer has shown thermal stability to 370°C by TGA (Fig. 3). The effects of thermal aging on polymer molecular weights, however, show it to be stable to rearrangement at 300°C, an improvement over the polymer containing pendent groups.

The thermal-oxidative stability of the backbone carborane polymer has been shown by TGA to be poor (240°C; Fig. 4). This is the same order of magnitude as for dimethylsiloxane polymer, and it indicates that oxidation occurs by reaction at silyl methyl groups.

Another series of *meta*-carboranyl siloxane polymers with excellent thermal stability has been studied (*16*). These polymers

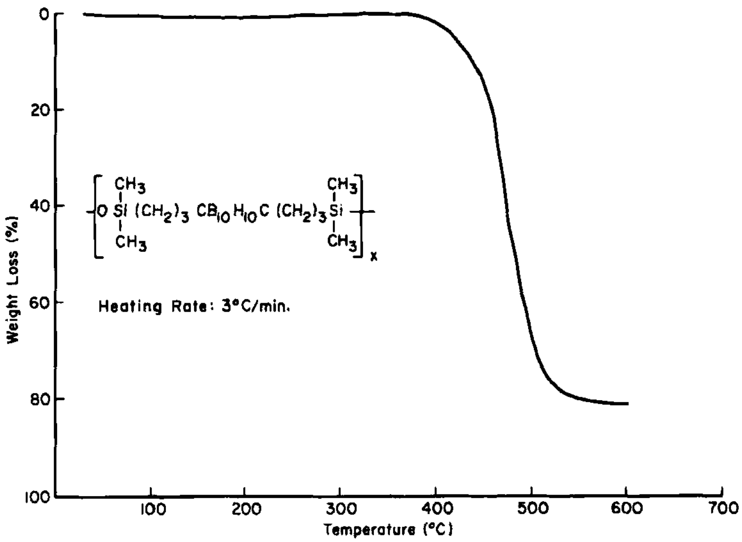


FIG. 3. Thermal gravimetric analysis of polycarboranylsilicone in N_2.

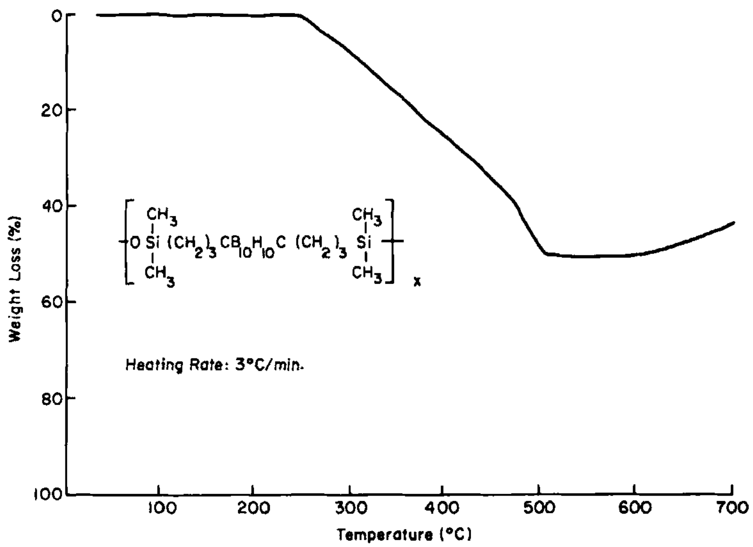
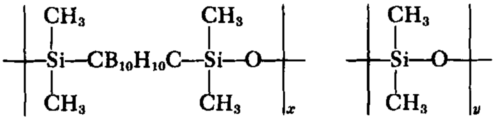


FIG. 4. Thermal gravimetric analysis of polycarboranylsilicone in air.

are prepared by the condensation of dichloro- and dimethoxysilanes with ferric chloride as catalyst. Their thermal and oxidative



$$\left[\mathrm{Si(CH_3)_2{-}CB_{10}H_{10}C{-}Si(CH_3)_2{-}O}\right]_x \quad \left[\mathrm{Si(CH_3)_2{-}O}\right]_y$$

stability was studied by means of differential calorimetry both in air and under nitrogen. Where $y = 0, 1, 2$ in the above structural formula the polymers were reported to be stable up to 500°C in an inert atmosphere (*16*). In air, however, only the polymers where $y = 0$ remained inert up to 450°C. The other two polymers reacted apparently at the $\mathrm{Si(CH_3)_2}$ groups bonded to the oxygen. The inductive effect of the carborane group adjacent to the silicon atoms apparently protected these silyl methyl groups from oxidation.

Carborane Benzimidazole Polymers

Two types of carborane benzimidazole polymer have been prepared, one containing an *o*-carboranyl group pendent to the chain and the other containing a *m*-carborane group in the polymer backbone. The former is prepared by allowing bromomethyl-*o*-carborane to react with the sodium salt of a benzimidazole polymer

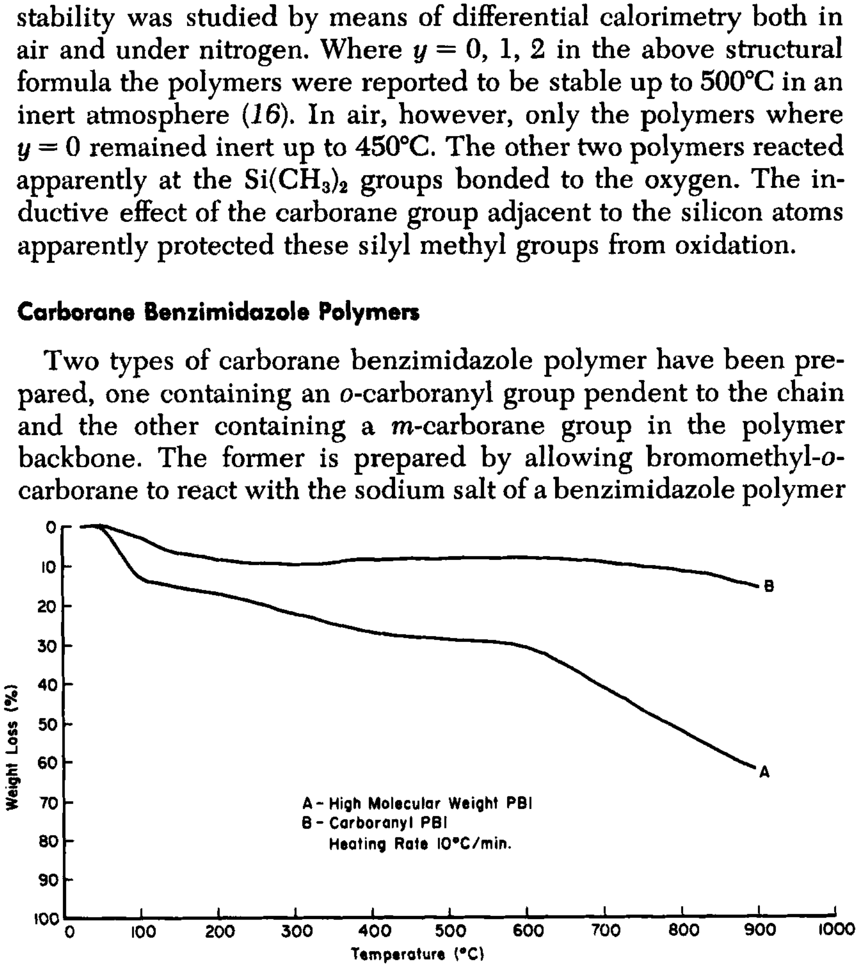


FIG. 5. Thermal gravimetric analysis curves for high-molecular-weight polybenzimidazole—$\mathrm{CH_2{-}\underbrace{C{-}CH}_{\substack{O\\ B_{10}H_{10}}}}$ in nitrogen.

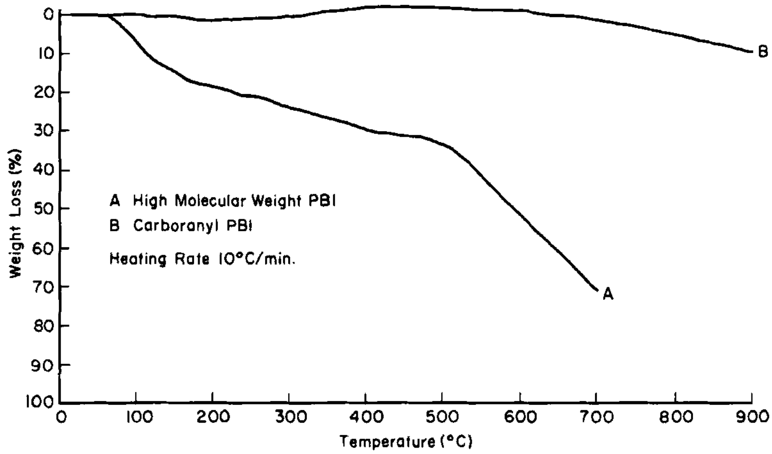
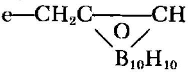


FIG. 6. Thermal gravimetric analysis curves for high-molecular-weight polybenzimidazole—CH_2C——CH in air.



$$CH_2\underset{\displaystyle B_{10}H_{10}}{\overset{}{C\!\!\underset{\diagdown\,O\,\diagup}{\text{———}}\!\!CH}}$$

(*13*). Approximately 50% of the benzimidazole hydrogens are replaced with methylene carborane groups. TGA data in nitrogen and in air show a substantial improvement in thermal stability when compared with the starting polybenzimidazole (Figs. 5 and 6). Clear films of this polymer on stainless steel and titanium substrates

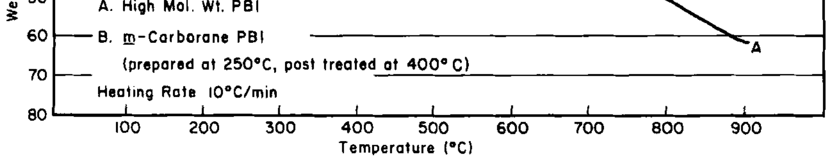
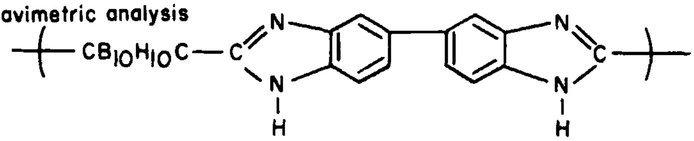


FIG. 7. Thermal gravimetric analysis in N_2 of



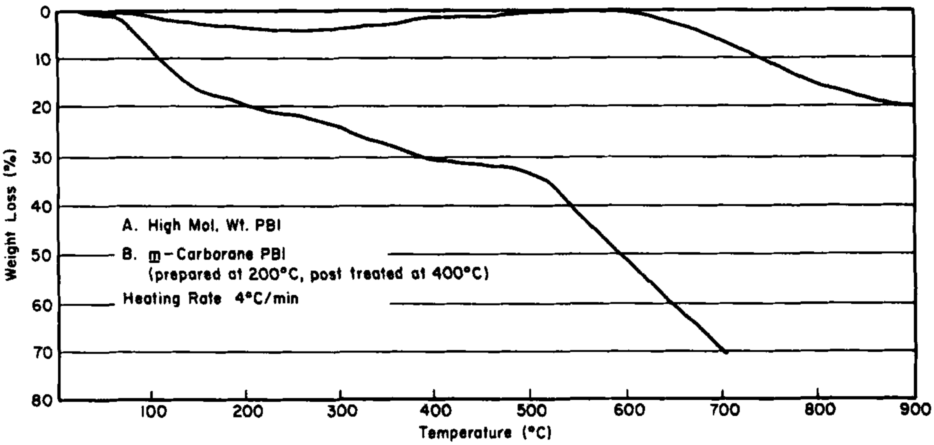
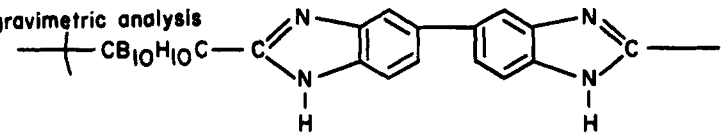
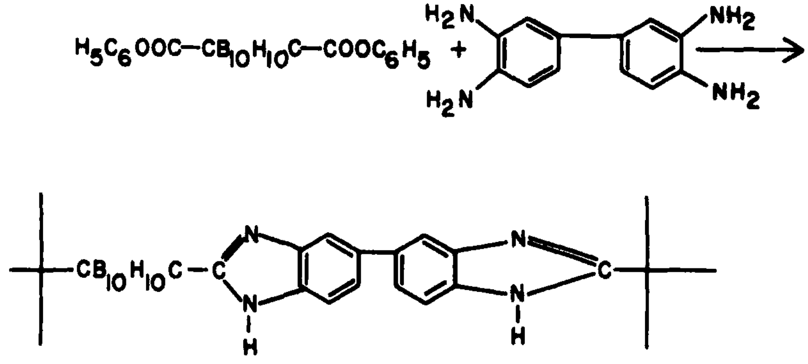


FIG. 8. Thermal gravimetric analysis in air of



have been prepared and examined at elevated temperatures in air. The coatings exhibited no visual change or change in dielectric strength after 10 hr at 427°C and were still intact but porous after 25-hr exposure (*15,17*).

The reaction of diphenyl-*m*-carborane dicarboxylate with 3,3′-diaminobenzidine yields a low-molecular-weight polybenzimidazole containing *m*-carborane in the polymer backbone (*14*). TGA data show this polymer to possess high thermal stability. Comparison of TGA curves for aromatic PBI (3,3′-diaminobenzidine and diphenylisophthalate) and carborane PBI indicate a distinct superi-



ority in thermal stability for the carborane product (Figs. 7, 8). The gain in weight in air was apparently due to oxidation of carborane to boric oxide. The fact that the weight gain was limited to 4% and that subsequent weight loss essentially leveled off at 20% indicate that the oxidation was limited and apparently occurred only at the exposed surface. The oxidized surface apparently formed a protective coating and prevented further oxidation. Some support for this theory is given by the isothermal TGA in air shown in Fig. 9.

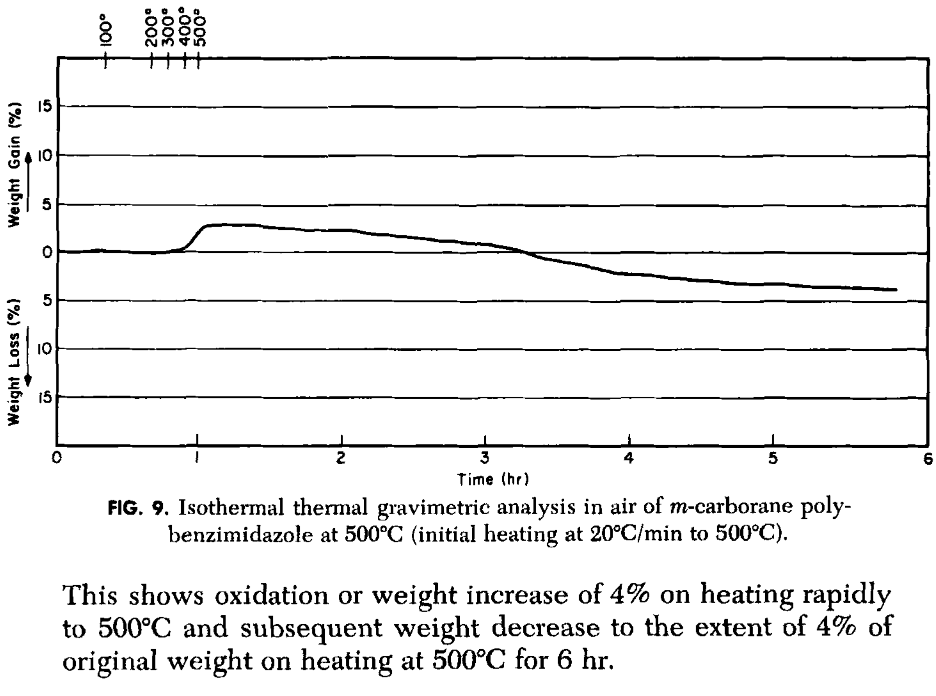
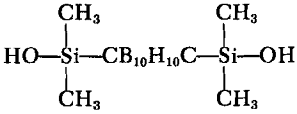


FIG. 9. Isothermal thermal gravimetric analysis in air of *m*-carborane polybenzimidazole at 500°C (initial heating at 20°C/min to 500°C).

This shows oxidation or weight increase of 4% on heating rapidly to 500°C and subsequent weight decrease to the extent of 4% of original weight on heating at 500°C for 6 hr.

DISCUSSION

The increase in thermal stability of siloxane polymers through incorporation of carborane groups in the polymer is attributed to its inductive effect. The following is presented to support this contention. It is known that dimethylsilane diol condenses so easily that it is difficult to isolate but that aromatic silanols are less reactive. Substitution of trifluoromethyl groups on the aromatic ring produces corresponding silanediols that are almost completely resistant to condensation even in contact with molten lead (327°C), which is a powerful catalyst (*18*). With only partial substitution of the aromatic ring with trifluoromethyl groups low polymers have been formed with considerable difficulty, and they are as resistant to hydrolysis and rearrangement as they are to condensation. Similarly, the inductive effect of a *m*-carborane group in the following silanediol prevented its successful polymerization (*16*).



$$\mathrm{HO{-}\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{Si}}}}{-}CB_{10}H_{10}C{-}\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{Si}}}}{-}OH}$$

Another consideration concerning the increase in thermal stability of the siloxane polymer containing the *m*-carborane group in the polymer backbone may be inhibition of helical coil formation by the backbone carborane group, removing the low-energy path to cyclic formation.

The increase in thermal stability of the benzimidazole polymers through incorporation of carborane groups is attributed to the inductive effect of the carborane group on stabilizing the imidazole ring.

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