JOURNAL OF APPLIED POLYMER SCIENCE VOL. 11, PP. 1979–1990 (1967)

Thermal Behavior of Dimethyl-*m*-carboranyl–Dimethylsiloxane Copolymers*

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Synopsis

The manner in which a series of silcarboranylene–siloxane polymers behave in air at elevated temperatures was investigated by thermogravimetric, isothermogravimetric, and differential thermal analyses techniques. Results indicate that methyl pendant groups on the polymers undergo thermal and oxidative degradations at temperatures under 600°C. Final weight losses of the polymers, however, are significantly lower than that shown by dimethylsiloxanes. The reduced volatility is attributed to the inhibition of thermooxidation by the *m*-carboranylene group in the polymer molecules. This protective influence decreases apparently as the distance between the carborane nucleus and the methyl groups increases.

INTRODUCTION

In the course of exploring the thermal resistance of new experimental polymers, several materials that contain a carborane nucleus in the main chain or pendant groups have been examined. A preceding article[1] described the results of studies made of the heat stability of organosiloxane copolymers containing methyl and *o*-carboranylbutyl pendant groups. This paper presents the results of investigation of a series of copolymers that have a *m*-carborane group in the main chains. [The designation of *m*-carborane for the 1,7-dicarbaclovododecaborane (12) structure rather than the previously assigned nomenclature of neocarborane[2,3] is used throughout this manuscript.]

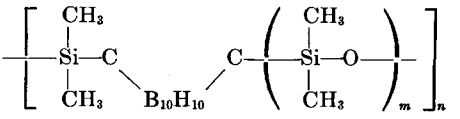
EXPERIMENTAL

Materials

Samples of three types of dimethylsilyl-*m*-carboranylene–dimethylsiloxane copolymers were examined as received from the Olin Mathieson Corp. Organics Division, New Haven, Conn. Their preparation and some

* Paper presented at the American Chemical Society Regional Meeting, Louisville, Kentucky, October 27–29, 1966.

of their properties are described elsewhere.[4] A general formula for the copolymers is:



where —C—$B_{10}H_{10}$—C— refers to the *m*-carborane nucleus, *n* is the number of repeating units, and *m* is 1, 2, and 3 for the copolymers designated herein as I, II, and III, respectively.

Methods

The thermogravimetric (TGA), differential thermal (DTA), and isothermogravimetric (IGA) analyses procedures used in this study were identical to those employed previously.[1]

Infrared absorption measurements over the 2.5–15.0 μ range were obtained from Nujol mulls as previously described.[1]

RESULTS AND DISCUSSION

Thermogravimetric Analysis

The results of TGA determinations in air are presented in Figure 1. These data show that the weight of copolymer I began to decrease at 250°C., increased slightly between 340 and 350°C., diminished once more in the range of 350–375°C., and then rose again at temperatures above 375°C. The combined weight losses of the sample were about 0.7%. This small decrease may have been due to the volatilization of some decomposition products or contaminants. The oxides of boron and silicon found deposited on the sample container at the end of the experiment suggest that the weight increases were produced as a result of thermal oxidation of the copolymer.

The rate of weight gain beginning at 375°C. reached a maximum at 460°C. This is very near the temperature at which it has been reported that the material undergoes a small, but sharp, exothermic change.[4] The rate of weight change then dropped to a lesser value at 475°C., attained a second peak value at 515°C., decreased at 535°C., and finally reached another maximum at 660°C. It is evident from these rate fluctuations that the thermal decomposition of copolymer I proceeds through more than one reaction.

When heated in air, copolymer II started to lose weight at 310°C. The decrease continued until a total loss of 1.9% was observed at 335°C. This loss corresponds to the rupture of one methyl group per gain of one-half oxygen atom. Of course, it is conceivable that the weight decreases may have resulted from the partial cleavage of dimethylsiloxane structures, by rupture of hydrogen atoms from the carborane nucleus, or through volatilization of impurities. At 335°C. the samples began to gain weight.

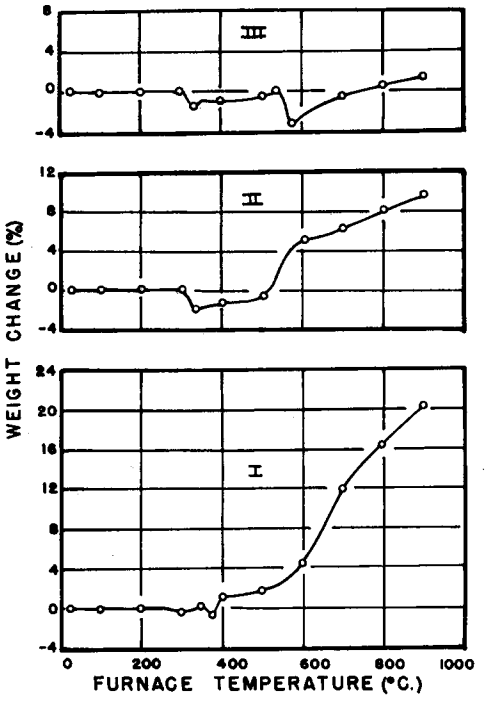


Fig. 1. TGA thermograms.

The rate of weight increase reached a maximum at 350°C., dropped off at 380°C., and then attained a second maximum at 410°C. These data parallel results obtained by differential scanning calorimetry.[4] The sample continued to gain weight in the temperature range of 500–900°C.

Initially, copolymer III behaved like copolymer II. The sample weight started to decrease at 310°C. until at 335°C. the loss was 1.4%. The decrease is equivalent to the net weight change obtainable from the scission of one methyl group and addition of one-half oxygen atom. The sample weight increased in the temperature range of 335–542°C., decreased again between 542 and 570°C., and then increased until the experiment was completed at 900°C. A maximum weight decrease of 3.3% was observed at 570°C. which coincides with the loss of two methyl groups per gain of one oxygen atom. The rate of weight gain at temperatures above 570°C. reached a maximum value at about 650°C. The same rate peak was observed in the thermograms from copolymers I and II. While it is possible that this may be the temperature at which oxidation of the carborane nucleus occurred at a maximum rate, this would have to be confirmed by additional experimental work. Such studies are under way.

Figure 2 presents semilogarithmic plots of the combined TGA weight losses measured as a function of the total number of methyl groups and siloxane units in the copolymer molecules. The linearity of these plots

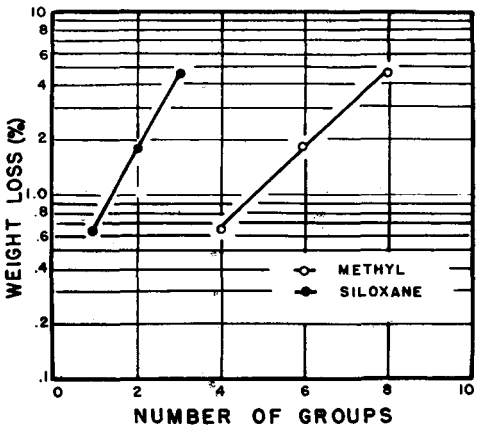


Fig. 2. Weight loss as a function of methyl groups and siloxane units.

indicates that the observed weight losses may be associated with the rupture of Si—C or Si—O bonds. From the small weight losses observed, it is considered more probable that Si—C cleavage was the predominant reaction.

It is interesting to note that, except for the initial 0.2% loss exhibited by copolymer I, small weight gains were observed just prior to each weight decrease. This suggests that these weight losses were the result of oxidation reactions rather than just thermal effects. Conventional dimethylpolysiloxanes are reported to undergo similar oxidation-induced weight losses when heated at elevated temperatures in air.[5–8]

Differential Thermal Analysis

The results of DTA measurements are given in Figure 3. The endothermic and exothermic deflections are in good agreement with previously reported differential scanning calorimetric measurements made at 500°C.[4] On the basis of the DTA thermogram obtained from a dimethylpolysiloxane oil,[9] the initial exothermic change exhibited by the copolymers in the temperature region of 250–450°C. can be reasonably associated with the oxidation of methyl groups. This conclusion is supported by TGA data which showed that oxidative weight gains occurred at these temperatures.

At about 510°C. copolymers II and III began to undergo a second exothermic transformation that reached a peak at approximately 550°C. and returned to the base line at about 600°C. Figure 4 presents a plot of the area beneath this peak as a function of the number of methyl groups and dimethylsiloxane structures in the copolymer molecules. The apparent linearity of these relationships indicates that this exotherm was due predominantly to the thermooxidative cleavage of methyl groups or siloxane linkages.

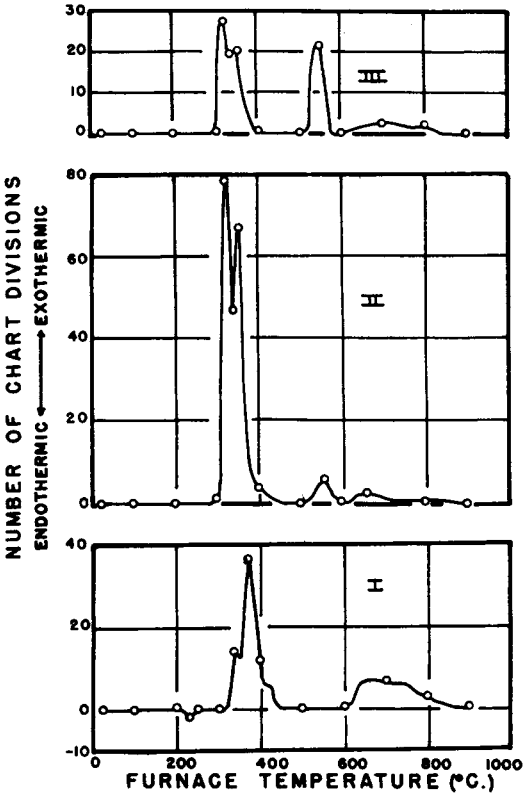


Fig. 3. DTA thermograms.

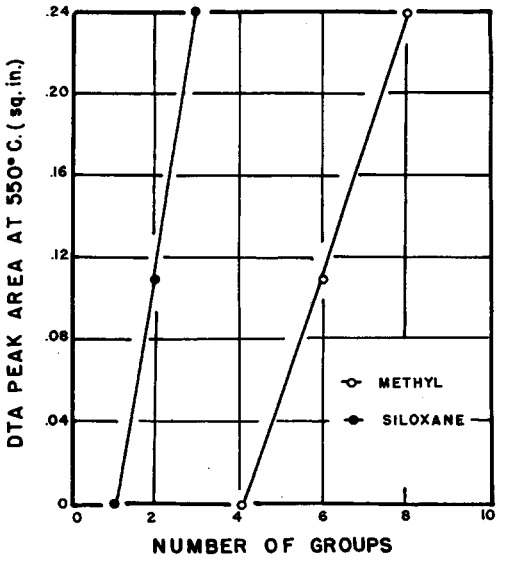


Fig. 4. DTA peak area as a function of methyl groups and siloxane units.

The copolymers showed a final broad exothermic change at temperatures ranging from about 600 to 850°C. It is suspected that this is the result of thermal oxidative decomposition of the carborane nucleus. Of course it also is possible that some methyl groups remained to undergo oxidation at these temperatures.

Isothermogravimetric Analysis

After being heated in air for 6 hr. at 300°C., a sample of copolymer I was transformed to a hard fused, resinous mass, while copolymers II and III became discolored, hard, and brittle. All of the copolymers became hard and embrittled when similarly exposed for 6 hr. at 500°C.

Figure 5–7 show the weight changes of the copolymers during isothermal heating in air at 300 and 500°C. These data indicate that at 300°C. copolymer I underwent a loss of 1.1% after 20 min. and then the sample weight remained virtually unchanged during the next 5.5 hr. Since the infrared absorption spectra from the residue and an unheated copolymer I sample appeared to be alike, it is considered that the weight decrease was probably due to the volatilization of contaminants rather than decomposition products. It thus appears that copolymer I is resistant to thermal and oxidative attack at 300°C. This is in accord with conclusions made from differential scanning calorimetry studies of this material.[4]

Copolymers II and III behaved similarly at 300°C., showing weight losses of 3.3 and 3.1%, respectively, during the first hour. These data together with results from TGA studies suggest that the weight decreases were the result of the rupture of one and two methyl groups from copolymers II and III, respectively. Additional evidence of methyl group cleavage was obtained from infrared spectroscopy measurements which showed that CH_3/B-H absorbance ratio (7.93/3.83 μ) was lower in the spectra from the IGA residues than in those from the original copolymers. It is interesting to note that the number of methyl groups that appear to

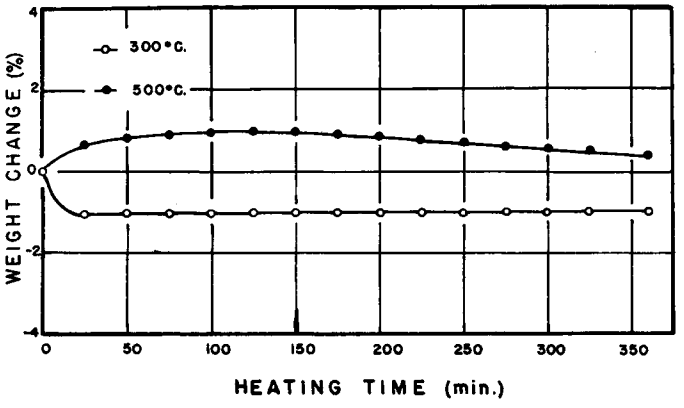


Fig. 5. IGA thermograms of copolymer I.

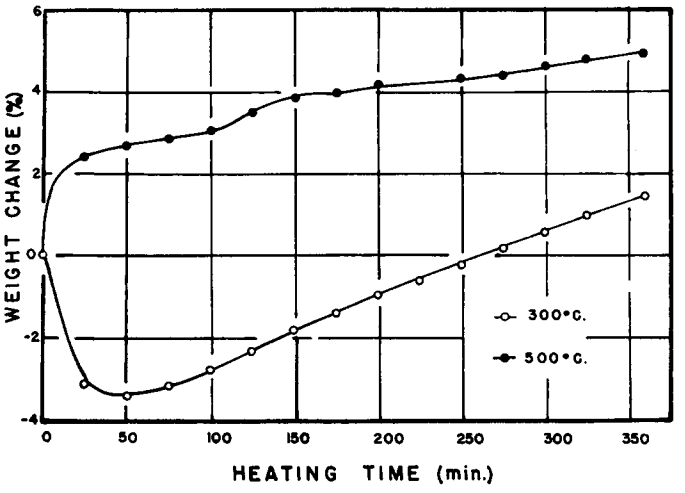


Fig. 6. IGA thermograms of copolymer II.

have ruptured conforms with the amount of $Si(CH_3)_2$ units of copolymers II and III that are not adjacent to a carborane group. This seems to indicate that the thermal and oxidative decomposition of $Si(CH_3)_2$ units is inhibited when they are bonded directly to the carborane configuration. This supposition is supported by the fact that copolymer I, which contains only $Si(CH_3)_2$ groups that are directly connected to a carborane nucleus, is apparently unaffected when heated for 6 hr. at 300°C. The stability of copolymer I may possibly be ascribed to the electron-withdrawing power of the carborane nucleus, the effect of which has previously been reported in the literature.[10] From the weight losses exhibited by copolymers II and III, it would seem that there is less of a protective influence on the de-

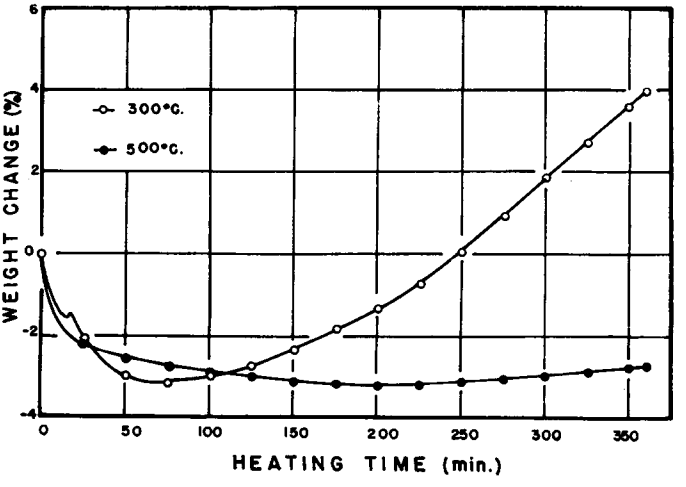


Fig. 7. IGA thermograms of copolymer III.

composition of $Si(CH_3)_2$ units that are not directly bonded to the carborane nucleus.

The weight gains observed from copolymers II and III subsequent to the weight losses are attributed to oxidation reactions. Because of the unusually good resistance of copolymer I to decomposition at 300°C., it is considered more likely that these weight increases can be attributed to the oxidation of methyl groups rather than of the carborane nucleus. The high resistance of the carborane group to oxidation has been reported by other workers.[11] In contrast to this, pendant methyl groups of siloxane polymers are known to oxidize when heated above 250°C.[1,5–8]

A comparison of the weight increase of each copolymer as a function of time is presented in Figure 8. These data indicate that during almost all of the heating period the gain in weight of copolymer II was linear at a rate of about 0.017%/min. On the other hand, the weight increase of copolymer III occurred in two stages with rates of gain of about 0.018 and 0.035%/min., respectively.

The observation of weight gains at 300°C. for copolymers containing dimethylsiloxane configurations is not usual. Although it has been known for some time that polymethylsiloxanes undergo thermal oxidation reactions, it has not been too clear until recently whether the methyl groups oxidize before or after they are ruptured from silicon atoms. In fact the earlier literature indicates that no instances are known where atmospheric oxidation of the methyl groups occurs while it is attached to silicon.[12] It is possible that this is generally true at room temperature; however, Scala and co-workers[7] have shown that considerable quantities of oxygen are consumed before any volatilization products are obtained when polysiloxanes are heated in air at 400°C. During the course of other investigations[1] it was established that polysiloxanes can undergo weight gains because of thermal oxidation before volatilization products become evident. Kuzminskiĭ and Goldovskiĭ[13] ascribe the cleavage of Si—O bonds of the

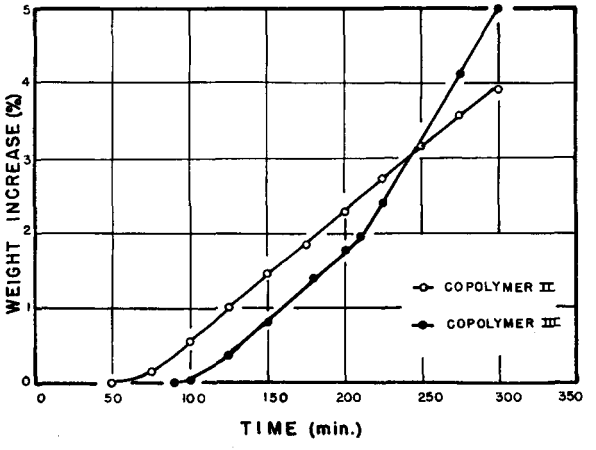


Fig. 8. Weight increase of copolymers II and III as a function of time.

main chain to the accumulation of reactive groups from the oxidation of methyl pendant units. In each of these studies, however, the oxidation period was brief, and it was followed almost immediately by the production of volatile decomposition materials. In contrast to this, weight loss was not observed during 5.5 hr. after the onset of weight gain of copolymers II and III.

Extensive investigations indicate that polarity and steric hindrance factors, bond energies, and inductive effects may markedly influence the behavior of materials. It has been suggested above that the electron-withdrawing power of the carborane nucleus prevented the rupture of methyl groups from silicon atoms to which it was directly bonded. Apparently, inductive effects were not sufficient to prevent methyl group cleavage from the silicon atoms not adjacent to the carborane nucleus. Since all of the latter type of methyl groups did not rupture, it would appear that factors other than electron-withdrawing power affected the behavior of copolymers II and III at 300°C. From the decrease in elasticity of these copolymers after the heating treatment, it may be inferred that new Si—O linkages were formed to replace the cleaved Si—C bonds. It is known that the polarity of Si—C bonds tends to decrease on addition of oxygen to the silicon atom.[14] It has been suggested that, for a given bond, the bond energy increases with decreasing polarity.[15] On this basis it would seem that the remainder of the methyl groups on silicon atoms not adjacent to a carborane nucleus did not cleave because of changes in the polarity and bond energy of the residual Si—C bonds. The literature also indicates that steric factors may have been an important influence in preventing the rupture of the residual methyl groups from copolymers II and III.[5,6,14] It is conceivable that a combination of these stabilizing factors permitted the thermal oxidation to occur at 300°C. without Si—C bond rupture.

It is of significant interest to note that the number of oxidation stages shown in Figure 8 corresponds with the quantity of methyl groups remaining in copolymers II and III that are not directly bonded to the carboranyl-silicon structures. Since it is known that dimethylsiloxane units are more susceptible to thermal oxidation than methylsiloxane structures, it is possible to assume from the similarity in the initial rate of weight gain of copolymer III and copolymer II that the residual methyl groups of the former material was bonded to different silicon atoms. Although each of the methyl groups would be expected to have equal susceptibility to oxidation, this would no longer be the case after oxidation of one of them. It is also suspected that the oxidized, but not ruptured, methyl group of copolymer III may have an inductive influence on the resistance of the remaining methysiloxane unit to oxidation. This would explain the change in rate observed during the latter stage of the 6 hr. heat treatment of copolymer III at 300°C. Studies of other polysiloxanes indicate that a good correlation can be made between thermal stability and the electron-donating or -withdrawing capacities of the substituent groups.[16] Investigations of other polymer systems have shown that the degradation mech-

anism involved when various ring-substituted polystyrenes are thermally degraded is greatly influenced by the electron densities of the substituent groups.[17]

At 500°C. in air copolymer I exhibited a weight increase of about 1% after 2 hr., and then weight decreases were observed. Copolymer II increased in weight throughout the 6 hr. heating period. After 3 hr., copolymer III showed a weight decrease of 3.2%, and then the weight increased during the following 3 hr.

The rate of weight gain appears to decrease with increasing methyl group content in each of the copolymer molecules. In addition, the rates of increase of copolymers II and III are much lower at 500°C. than at 300°C. Since reactions are expected to occur more rapidly at higher temperatures, the results obtained at 500°C. seem to be anomalous. It should be noted, however, that at 300°C. all of the copolymers displayed some volatility before weight increases were observed, while at 500°C. only copolymer III behaved in this manner. It is quite probable that a large weight loss actually did occur at the higher temperature, but that such a decrease was most likely masked by even larger weight increases, due possibly to the oxidation of residual methyl groups. From the more normal behavior of copolymer I, which displayed a higher rate of weight increase at 500°C. than at 300°C., it is believed that the residual methyl groups were connected to silicon atoms adjoining the carborane nucleus. The volatility of copolymer III before the event of weight increase at 500°C. seems to imply that the stabilizing influence of the *m*-carborane configuration decreases as the distance of the methyl groups from this structure increases.

SUMMARY

These studies indicate that at temperatures below 600°C. the silcarboranylene–siloxanes are susceptible to oxidation reactions similar to that of the more conventional dimethylpolysiloxanes. The silcarboranylene–siloxanes, however, exhibit much lower volatility losses than the polydimethylsiloxanes. This appears to be attributable to the stabilizing influence of the *m*-carborane group on the thermal oxidative decomposition of methyl groups, possibly in a manner similar to that of the *p*-phenylene structure in silphenylene, siloxane polymers.[18] The inhibiting effects of the carborane nucleus seem to be related to the proximity to the methyl group, the pendant groups attached to silicon atoms that are adjacent to the *m*-carborane group receiving more protection than those further away. Results also suggest that the carborane nucleus probably undergoes thermal oxidation at temperatures above 600°C.

The authors are indebted to E. A. Bukzin of the Naval Ship Systems Command and W. B. Shetterly of the Naval Ship Engineering Center, Washington, D.C., for sponsoring this work.

The opinions or assertions contained in this paper are the private ones of the author and are not to be construed as official or reflecting the views of the Naval Service at large.

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Résumé

La facon suivant laquelle une série de polymères silcarboranylène-siloxaniques se comportent à l'air à température élevée a été étudiée par thermogravimétrie, isothermogravimétrie et par différentes techniques thermoanalytiques différentielles. Les résultats indiquaient que les groupes latéraux méthylés sur les polymères subissent des dégradations thermiques et oxydatives à des températures en-dessous de 600°C. Les pertes en poids finales des polymères, toutefois, sont significativement plus basses que celles montrées par les diméthylsiloxanes. La volatilité réduite est attribuée à l'inhibition de la thermooxydation par le groupe *m*-carboranylène dans les molécules de polymères. Cette influence protectrice décroissait apparemment lorsque la distance entre le noyau carboranyle et le groupe méthyle augmentait.

Zusammenfassung

Das Verhalten einer Reihe von Silcarboranylen-Siloxyanpolymeren in Luft bei erhöhten Temperaturen wurde mittels thermogravimetrischer, isothermogravimetrischer und differentialthermoanalytischer Verfahren untersucht. Die Ergebnisse zeigen, dass an den Polymeren anhängende Methylgruppen bei Temperaturen unter 600°C. thermisch

und oxydativ abgebaut werden. Die Gesamtgewichtsverluste der Polymeren sind aber merklich niedriger als bei Dimethylsiloxanen. Die verringerte Verflüchtigung wird auf eine Inhibierung der thermischen Oxydation durch die *m*-Carboranylengruppe im Polymermolekül zurückgeführt. Diese Schutzwirkung nimmt offenbar mit steigendem Abstand zwischen Carborankern und den Methylgruppen ab.

Received November 11, 1966
Revised March 14, 1967
Prod. No. 1599