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A COMPARISON OF FIVE
SILOXANYLCARBORANE POLYMERS

By
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7 DECEMBER 1970

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Prepared by:
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ABSTRACT: Thermal properties of five structurally different siloxanylicarborane polymers are compared. Two polymers contain B₁₀-carborane groups, two B₅ groups, and one a B₈-carborane group. Their polymer decomposition temperatures (ranging from 440 - 550°C) depend on their chemical structure. Polymers containing the B₁₀-carborane moiety are thermally the most stable. They also show a longer retention of flexibility upon exposure to 250°C. These polymers show potential for high temperature rubbers.

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A COMPARISON OF FIVE SILOXANYLCARBORANE POLYMERS

This report contains a comparison of thermal and solubility properties obtained on five elastomeric polymers developed under Office of Naval Research sponsorship. The data, based on small laboratory samples, are limited and were obtained on pure, unfilled polymers. This work was done in FY 1969 on Task NOL 278, Assessment of Polymers, funded by ONR.

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By direction

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INTRODUCTION

In the search for new high temperature elastomers, the Navy has supported a large research effort on carborane chemistry. At this time, several polysiloxanyl-carboranes have shown potential as rubbery materials for high temperature use where other elastomeric materials fail.

Comparative data were obtained on five research samples supplied by Olin, Inc., Dr. R. E. Williams (Chemical Systems, Inc.), and Dr. B. F. Hawthorn (UCLA). The polymers were all prepared under Navy contracts.

The properties were determined on the polymers without fillers, oxidation inhibitors, or other protective additives. Their decomposition temperatures ranged from 440 to 550°C, depending on the chemical structure. Polymers containing the B₁₀-carborane cage showed the best thermal stability.

EXPERIMENTAL

Polymer Properties

The inherent and intrinsic viscosities of the polymers were obtained by means of an Ubbelohde viscosimeter in toluene at 30°C ± 0.05°C.

The solubilities of the polymers were determined in 18 different solvents. They were submerged for 24 hours in the solvents (at about 1% concentration) which were frequently agitated.

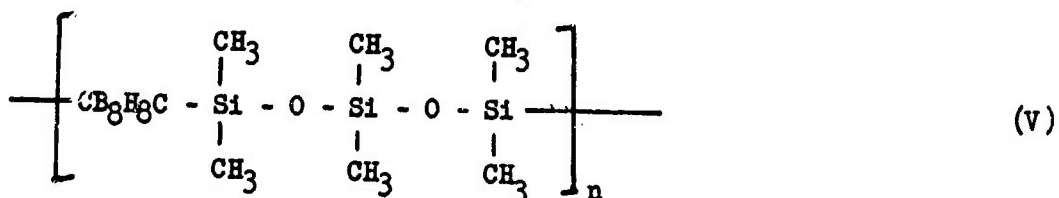
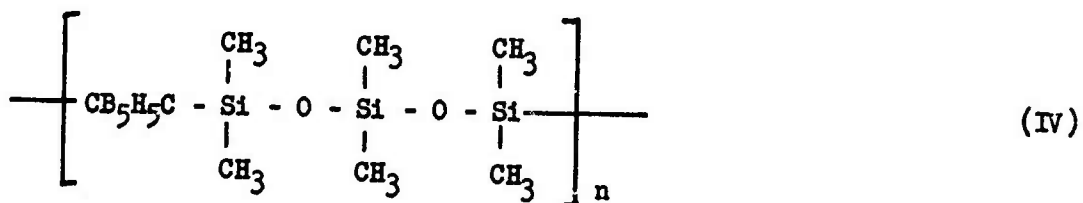
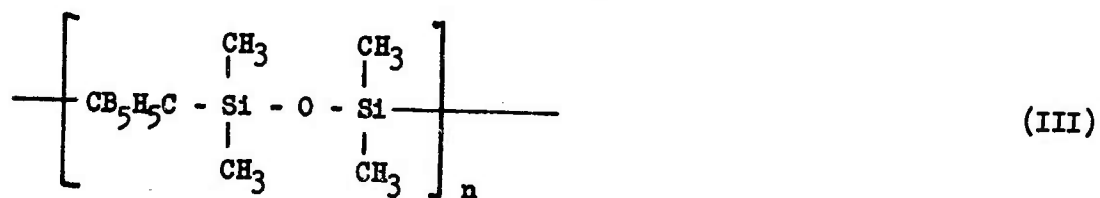
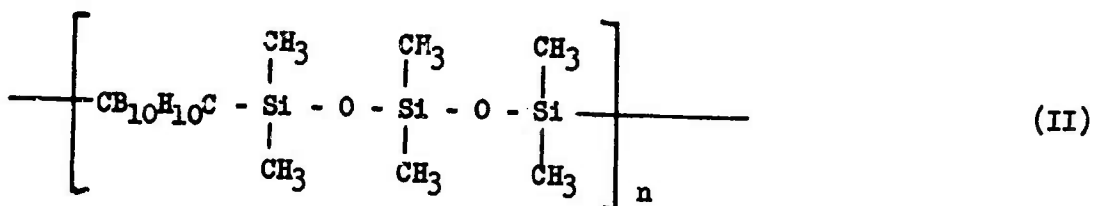
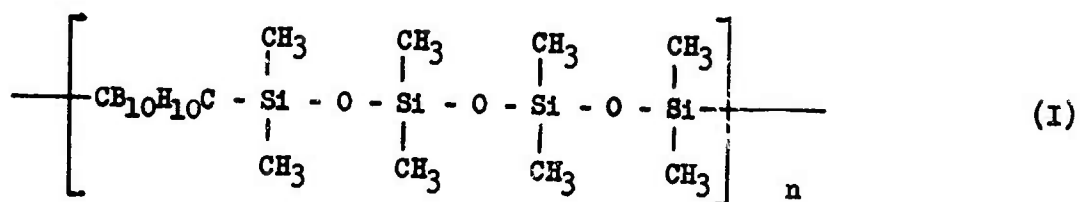
The thermogravimetric analysis (TGA) was run at a heating rate of 5°C/min in vacuum, using an Ainsworth electronic vacuum balance. The polymer decomposition temperature (PDT) is defined at the intersection of the 100% weight retention (horizontal) line with a line drawn tangent to the TGA curve at the point of maximum rate of decomposition.

The determination of weight change under isothermal conditions was carried out in static air at 350 and 400°C.

The dielectric loss measurement of polymers I, II, and IV was obtained from films. The experimental details for obtaining dielectric loss at varying temperatures are described in an earlier report (NOLTR 69-120). The heating rate was 5°C/min in all cases.

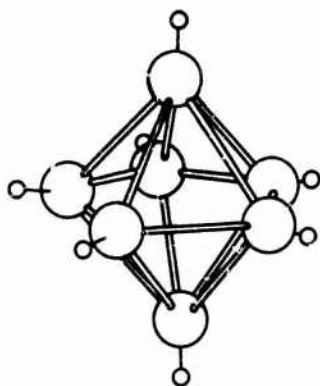
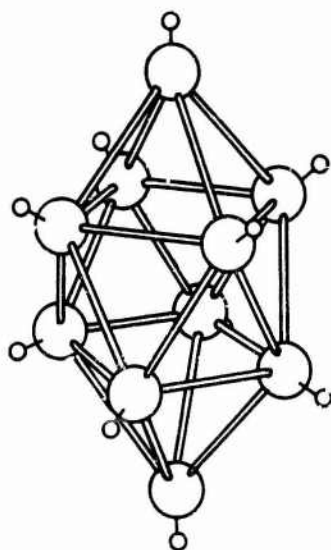
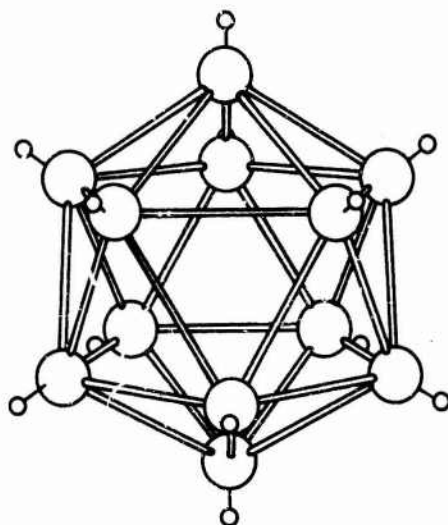
RESULTS AND DISCUSSION

The comparative data on a limited number of properties of five different siloxanylcarborane polymers are cited herein. The structures of these polymers differ in (a) size of the carborane cages, and (b) in the number of siloxanyl units linking these cages. The reported structures of these polymers are as follows:



where $\text{CB}_{10}\text{H}_{10}\text{C}$ -, $\text{CB}_8\text{H}_8\text{C}$ -, and $\text{CB}_5\text{H}_5\text{C}$ - indicate the following carborane cage structures:

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Polymers I and III had a waxy consistency. Polymers II and IV were rubbery. Polymer V was a tough solid after having been cured at 250°C. The structures II, IV and V given above must be considered idealized. From the solubility data given in Table 1, it is apparent that they are crosslinked to some extent, while Polymers I and III are linear. The latter are soluble in a number of aliphatic and aromatic hydrocarbons. The inherent viscosities (Table 2), however, indicate a low molecular weight which could explain their lack of strength.

The results of thermogravimetric analysis in vacuum at a heating rate of 5°C/min are given in Figure 1 and Table 3. The highest thermal stabilities were found for Polymers I and II (both polymers with B₁₀ cages). The rate of weight loss at the temperature of maximum rate of decomposition is dependent on the number of siloxanyl units linking the carboranes. The rate is fastest for Polymer I with three -Si-O- linkages and smallest for Polymer III with only one -Si-O- linkage. The residue remaining at 800°C is obviously dependent on the number of methyl side groups.

Change in weight at isothermal conditions was determined at 350 and 400°C in static air (Figures 2 and 3). In Figure 2, we observe that all polymers gain weight, indicating oxidation and/or uptake of moisture. The break in the curves indicates the increase in weight after decomposition at 350°C when the polymers were allowed to remain at room temperature for two days in open air. The decomposed materials evidently become quite hygroscopic.

At 400°C a different behavior was observed (Figure 3). Polymers with the B₅ cages gained weight from the beginning, while those with B₁₀ cages lost weight. Continuing the heat exposure over 1000 hours showed, however, that these latter polymers finally increase in weight also. It appears, therefore, that there are two competing reactions; first, decomposition of the dimethyl-siloxanyl part of the polymer leading to loss of methyl groups or small chain segments, and, second, oxidation of the carborane cage indicated by a weight increase. Depending on the relative rates of these reactions, the polymer may first lose weight and then later gain, or it may gain weight from the beginning. Even if the weight does not change for a long time, as can be seen with Polymer V, it does not necessarily mean that decomposition is not taking place.

The dielectric loss change (at 1000 Hz) with temperature of Polymers I, II and IV are shown on Figures 4, 5 and 6. The first two curves were exactly reproducible, even after heat curing to 350°C; the third was not reproducible, since additional curing had occurred on heating. From comparison with other polymers, the glass transition temperature (T_g) is very close to the onset of the lower temperature branch of the peak rather than to its maximum. For Polymer II this is -27°C, which is close to the value of -29°C published by Olin. Polymer I has a T_g of -50°C. The T_g of Polymer III (cured at 250°C for 30 minutes) is apparently below -85°C. (This is as low as the present setup of our instrument allows us to go.)

Coating properties were determined for Polymers I, II, and III. Polymer I was tested as a thin slice (cut with a microtome), while Polymers II and III were cast onto aluminum foil. They were exposed to air at 250°C, and their creasability was checked from time to time by bending sharply at 180°. The

point in time when the films became brittle was defined as the limit of creasability. For Polymer I, this was 550 hours; for Polymer II, 480 hours, and for Polymer III, less than 16 hours.

Stability under high relative humidity was tested by exposing polymer samples to 80°C at 95% relative humidity over a period of 700 hours. No visible change could be observed.

CONCLUSIONS

The thermal properties reported here are probably not the best that may be obtained with these polymers. Anti-oxidants, modification in crosslinking, and other fabrication parameters may improve upon these polymers. From the properties of these polymers, particularly TGA and film creasability, it appears that those with B₁₀ cages are thermally more stable than those with smaller carborane cages in the chain.

RECOMMENDATIONS

It appears that the greatest potential of the siloxanylcaborane polymers is in their use as high temperature elastomers and rubbers. A number of fabrication parameters will have to be solved. Problem areas are perhaps heat stable crosslinking systems and crystallization, which could embrittle the rubbers.

TABLE 1

SOLUBILITIES OF SILOXANYLCARBORANE POLYMERS

	<u>Polymer I^a</u>	<u>Polymer II^a</u>	<u>Polymer III^a</u>	<u>Polymer IV^a</u>	<u>Polymer V^b</u>
Ethylacetate	Soluble	Insoluble	Insoluble	Insoluble, Swelling	Insoluble
Carbon Tetrachloride	Soluble	Insoluble	-	Insoluble, Swelling	Insoluble
Chloroform	Soluble	Insoluble	Soluble	Insoluble, Swelling	Insoluble
Tetrachloroethane	Soluble	Insoluble	Soluble	Insoluble, Swelling	Insoluble
Petroleum Ether	Soluble	Insoluble	Soluble	Insoluble, Swelling	Insoluble
Benzene	Soluble	Insoluble	Soluble	Insoluble, Swelling	Insoluble
Acetone	Turbid	Insoluble	Insoluble	Insoluble	Insoluble
Dioxane	Turbid	Insoluble	Insoluble	Insoluble, Swelling	Insoluble
Dimethylacetamide	Turbid	Insoluble	Insoluble	Insoluble, Swelling	Insoluble
Pyridine	Soluble	Insoluble	Insoluble	Insoluble, Swelling	Insoluble
M-Cresol	Insoluble, Swelling	Insoluble	Insoluble	Insoluble, Swelling	Insoluble
Cyclohexane	Soluble	Insoluble	Soluble	Insoluble, Swelling	Insoluble
Toluene	Soluble	Insoluble	Soluble	Insoluble	Insoluble
Chlorobenzene	Soluble	Insoluble	Soluble	Insoluble, Swelling	Insoluble
Xylene	Soluble	Insoluble	Soluble	Insoluble	Insoluble
Nitrobenzene	-	Insoluble	Soluble	Insoluble	Insoluble
Anisol	Soluble	Insoluble	Soluble	Insoluble	Insoluble
Cyclohexanone	-	Insoluble	-	Insoluble, Swelling	Insoluble

a Sample as received from source.

b After evaporation of solvent and curing at 250°C.

TABLE 2
VISCOSITIES OF SILOXANYLCARBORANE POLYMERS

	<u>Polymer I</u>	<u>Polymer II</u>	<u>Polymer III</u>	<u>Polymer IV</u>	<u>Polymer V</u>
Inherent Visc. at 0.5 g/100 ml [η] (dl/g)	0.18	Insoluble	0.34	Insoluble	Insoluble ^a
Intrinsic Visc. [η] (dl/g)	0.20	Insoluble	0.60	Insoluble	Insoluble ^a

a Insoluble after evaporation of solvent and curing at 250°C

TABLE 3
TGA OF SILOXANYLCARBORANE POLYMERS

<u>Polymer No.</u>	<u>PDT (°C)</u>	<u>Temp. Max. Decomposition (°C)</u>	<u>Max. Rate of Decomposition (% per min)</u>	<u>Residue (%)</u>
I	550	563	3.8	59
II	540	560	1.3	74
III	460	515	0.45	84
IV	450	480	1.9	70
V	440	530	1.3	65

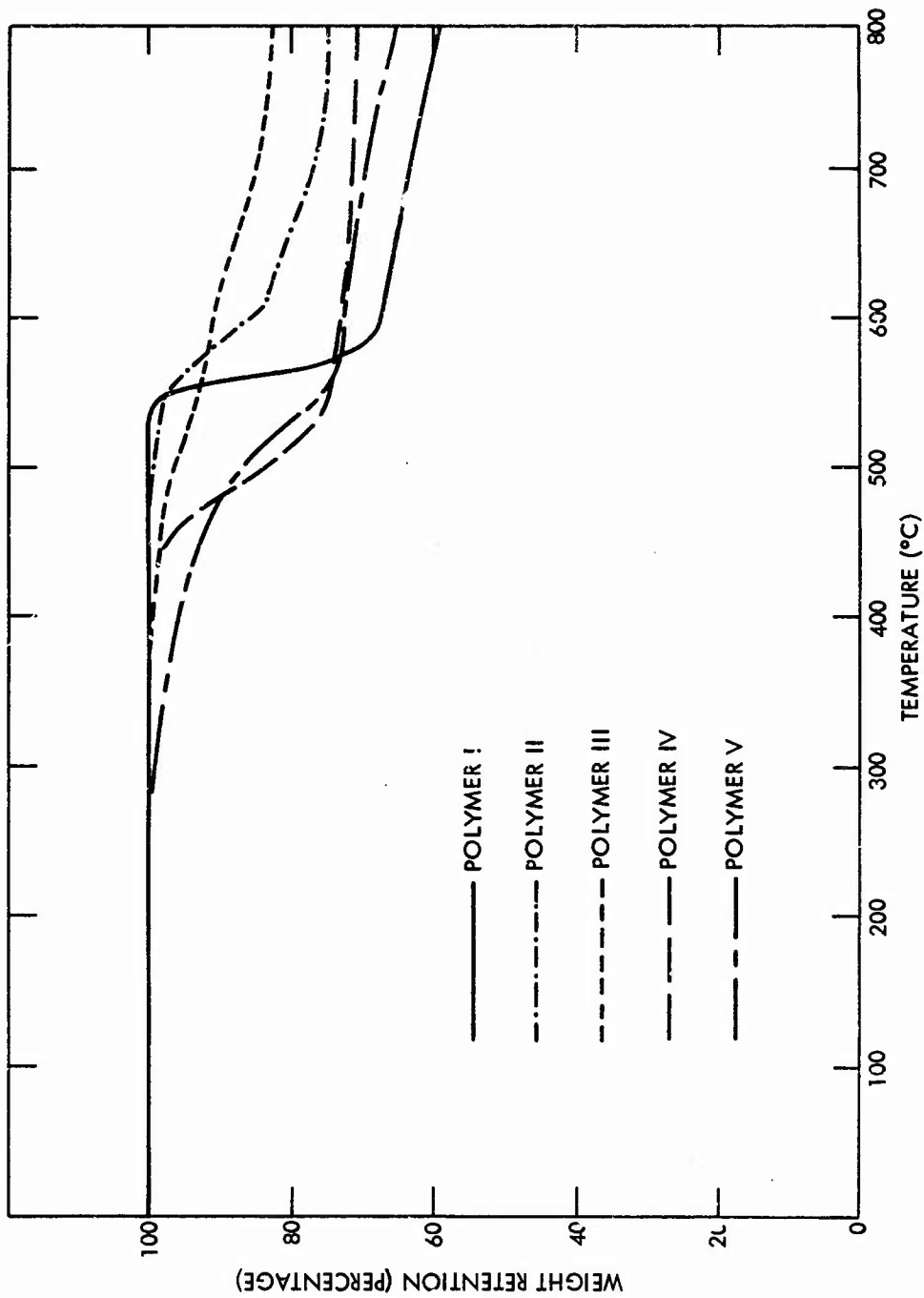


FIG. 1 TGA OF SILOXANYLCARBORANE POLYMERS

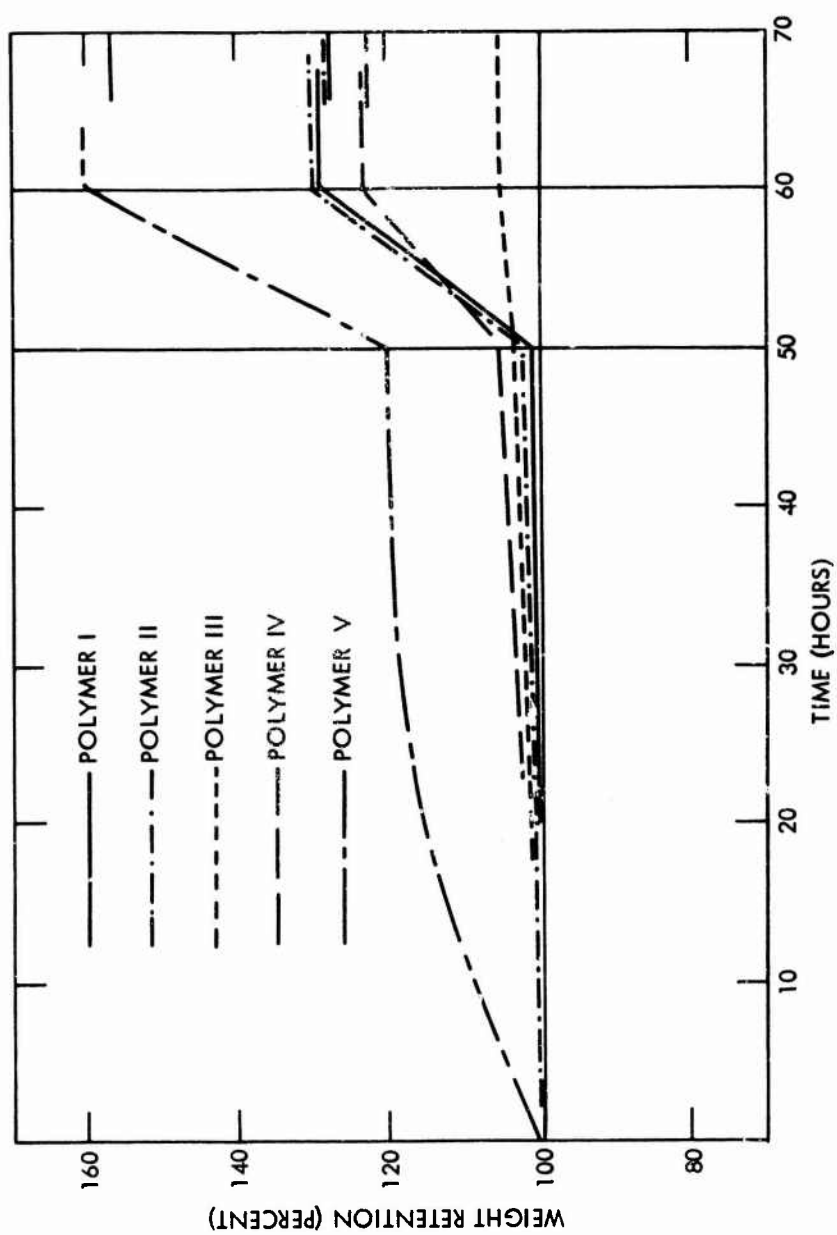


FIG. 2 ISOTHERMAL WEIGHT CHANGES OF SILOXANYLCARBORANE POLYMERS IN AIR AT 350°C

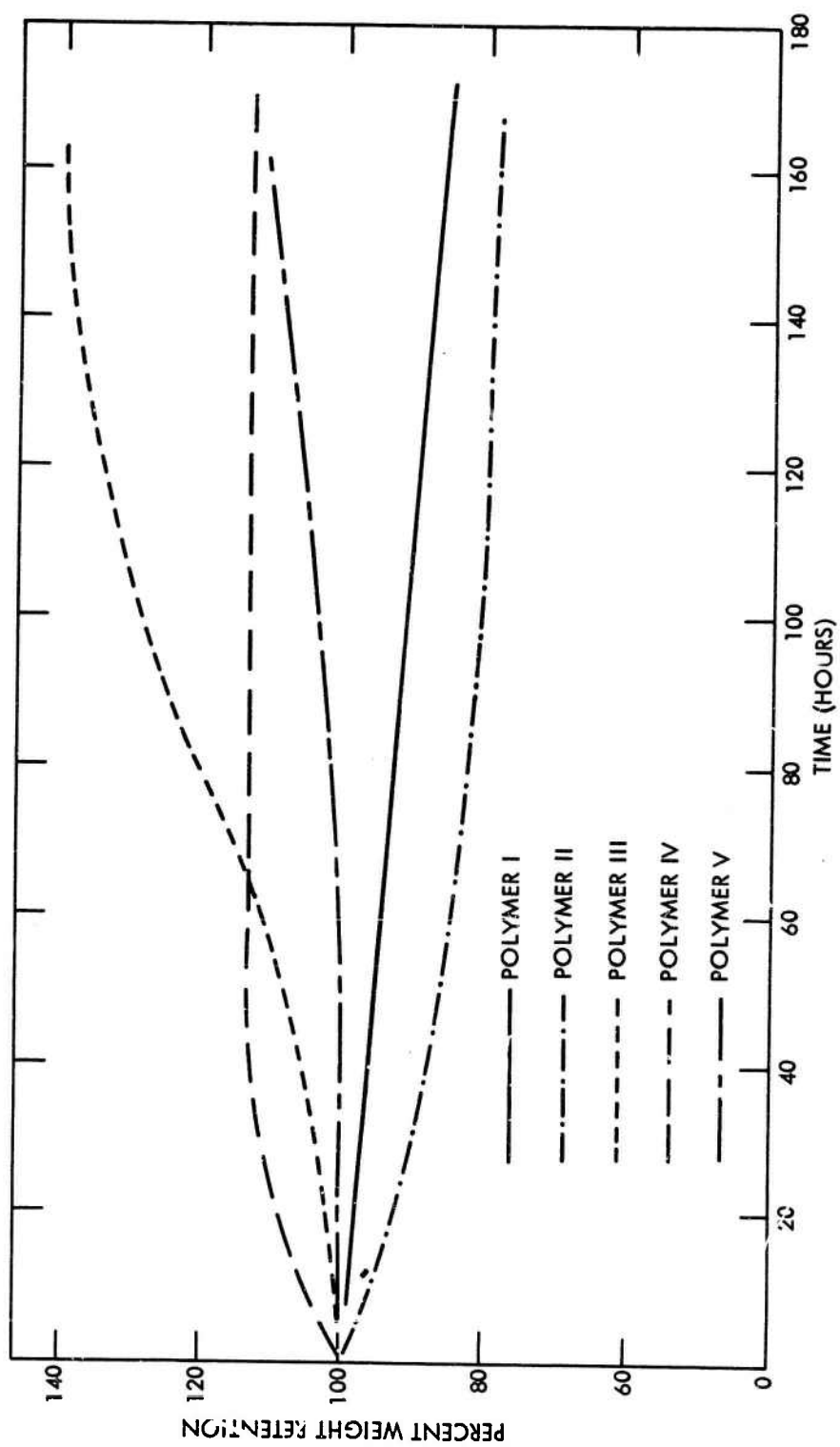


FIG. 3 ISOTHERMAL WEIGHT CHANGE OF SILOXANYLCARBORANE POLYMERS AT 400°C IN AIR

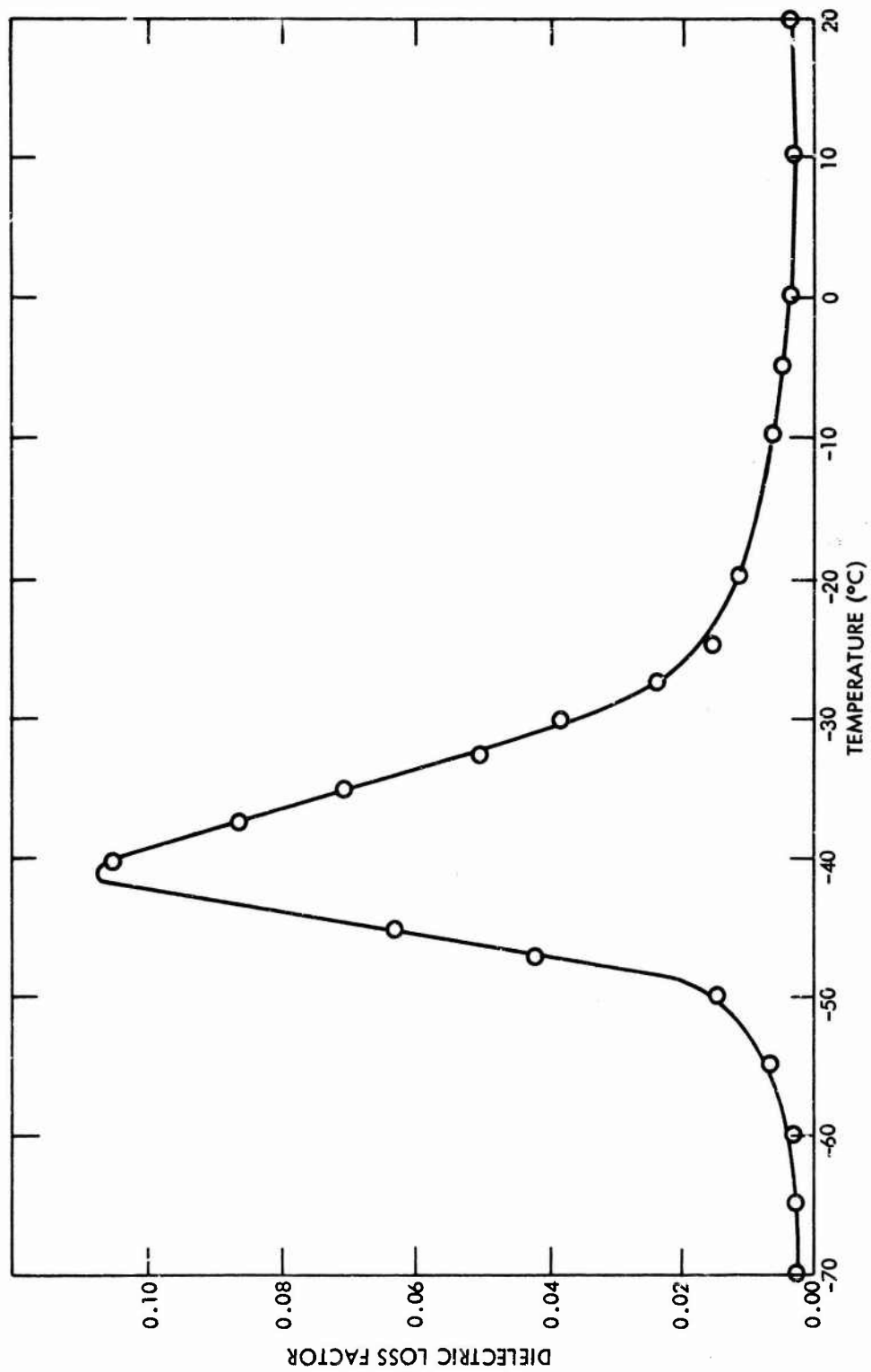


FIG. 4 DIELECTRIC LOSS OF POLYMER I (CURED AT 250 AND 350°C)

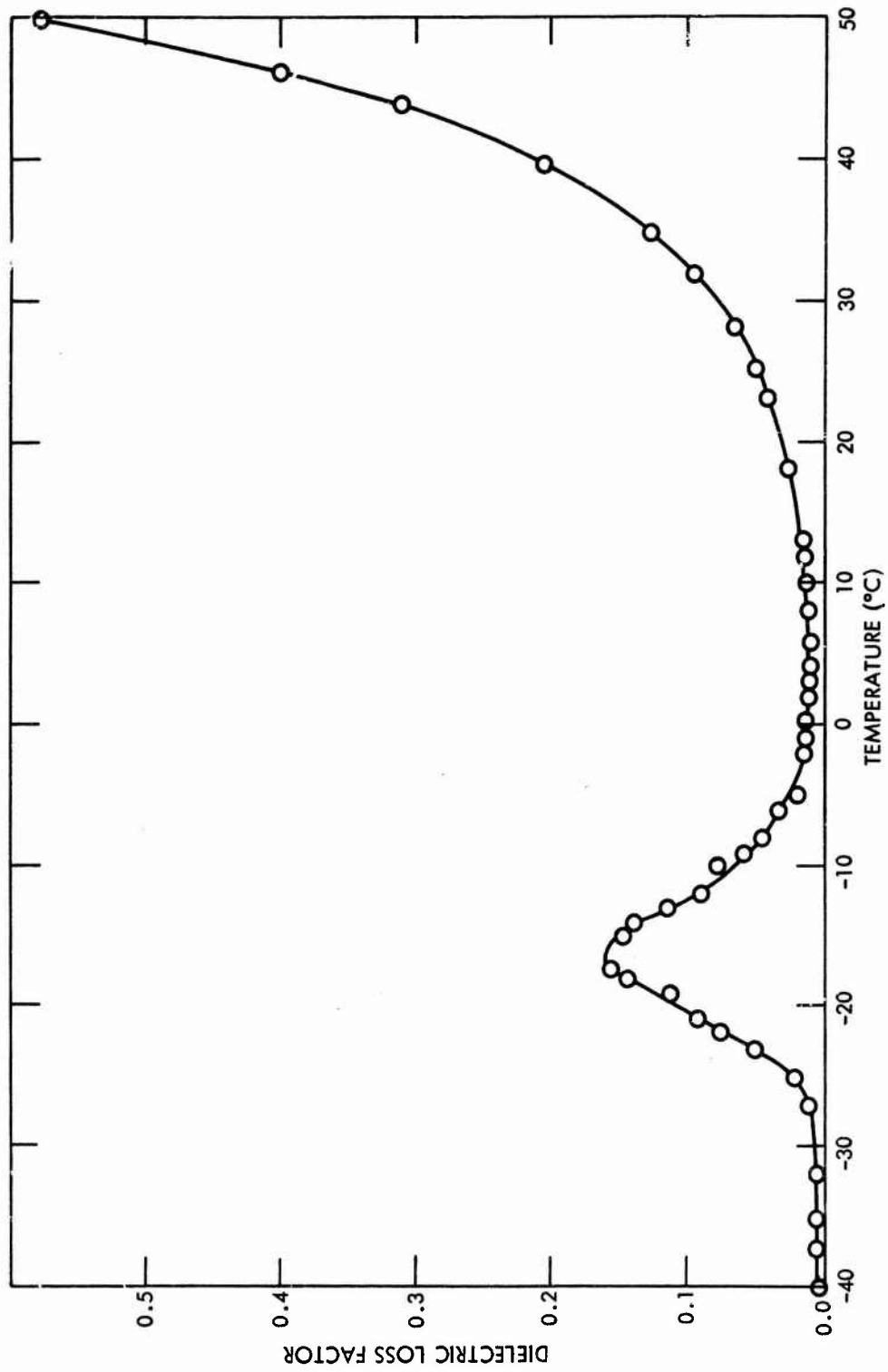


FIG. 5 DIELECTRIC LOSS OF POLYMER II

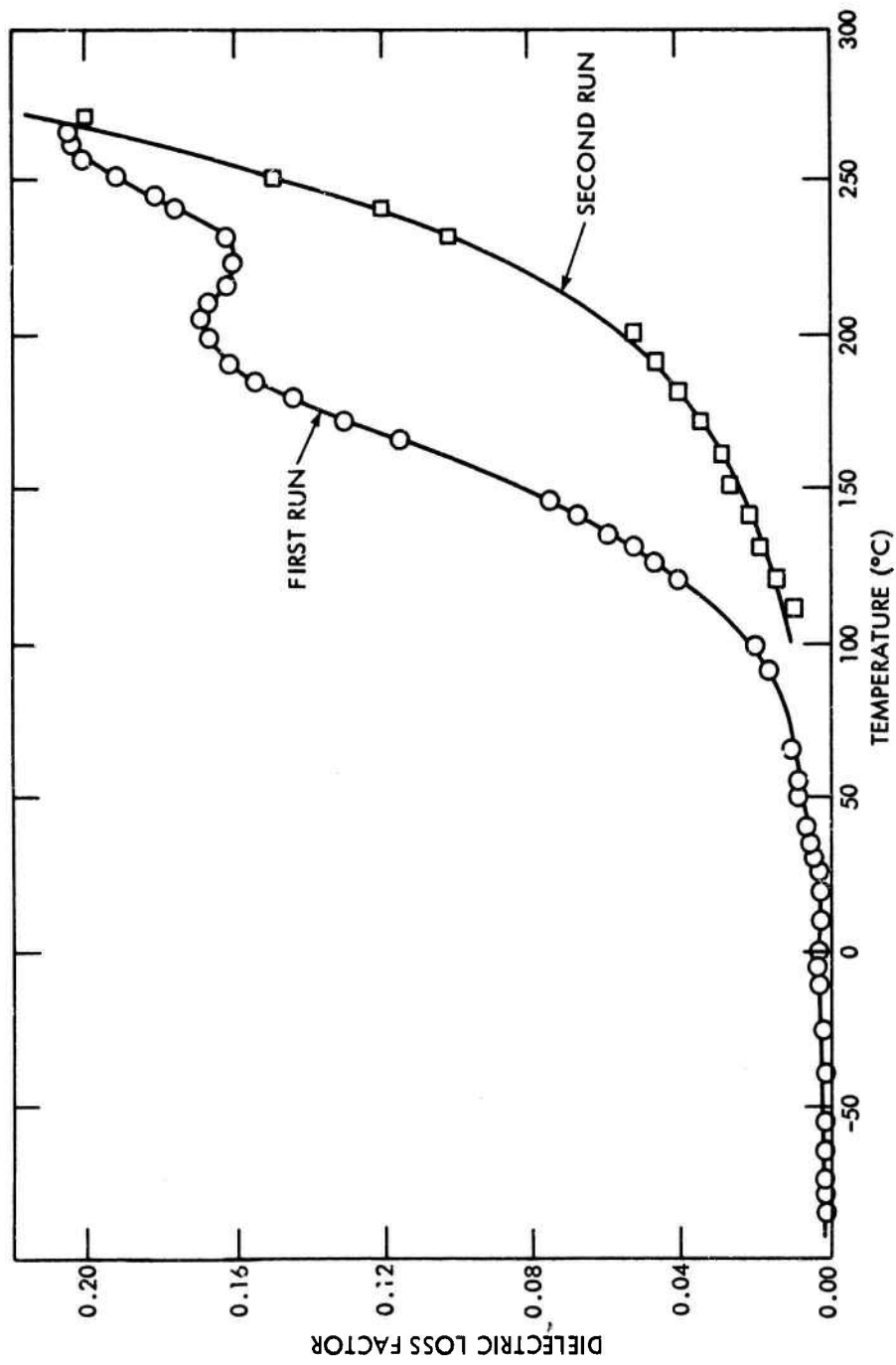


FIG. 6 DIELECTRIC LOSS OF POLYMER IV (CURED AT 250°C)

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