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D2-'META'-CARBORANE-SILOXANES

IV. SYNTHESIS OF LINEAR, HIGH MOLECULAR WEIGHT POLYMERS

UNION CARBIDE CORPORATION,
TARRYTOWN, NEW YORK

5 MARCH 1976

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D_2-meta-Carborane-Siloxanes. IV.
Synthesis of Linear, High Molecular Weight Polymers

by

E. Hedaya, J. H. Kawakami, G. T. Kwiatkowski, P. W. Kopf
D. W. McNeil, D. A. Owen, E. N. Peters, and R. W. Tulis

March 5, 1976

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A new facile route to linear, high molecular weight D_2-meta-decacarborane-siloxanes was developed based on the condensation reaction between bis-ureidosilanes and carborane disilanol. By using nmr to monitor the reaction stoichiometry, polymers with molecular weight $\geq$250,000 have been prepared. Moreover, because of the mild reaction conditions, structural modifications of the polymer backbone have been readily achieved. These linear high molecular weight polymers overcome the fabrication difficulities (over)

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D_2-*meta*-CARBORANE-SILOXANES. IV. SYNTHESIS OF LINEAR, HIGH MOLECULAR WEIGHT POLYMERS

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SYNPOSIS

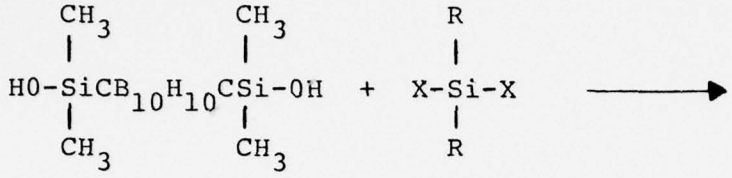
A new facile route to linear, high molecular weight D_2-*meta*-decacarborane-siloxanes was developed based on the condensation reaction between bis-ureidosilanes and carborane disilanol. By using nmr to monitor the reaction stoichiometry, polymers with molecular weight $\geq$250,000 have been prepared. Moreover, because of the mild reaction conditions, structural modifications of the polymer backbone have been readily achieved. These linear, high molecular weight polymers overcome the fabrication difficulities encountered in previously prepared D_2 polymers.

INTRODUCTION

The development of carborane-siloxane polymers in the early 1960's was a major breakthrough in the search for a high-temperature performance elastomer.[1] Incorporation of the carborane moiety into the siloxane backbone significantly enhanced overall thermal stability. A review of the carborane-siloxane polymer literature indicates that the D_2-*m*-carborane-siloxanes should possess the optimum combination of high temperature and elastomeric properties.[2] However, serious fabrication and vulcanization difficulities prevented exploitation of previously reported D_2-*m*-carborane-siloxanes.[3]

These difficulities were related to the mode of polymer synthesis which involved a ferric chloride catalyzed condensation of a chlorosilane with an alkoxysilane.[4] The ferric chloride induced a crosslinking process in the final reaction stage to afford a network polymer rather than a truly linear polymer.[5]

To obviate the deleterious effects of ferric chloride catalyst used in previous routes to linear D_2-carborane-siloxanes (1), a process based on the condensation of carborane disilanol (2) with a reactive silane comonomer (3) was chosen.



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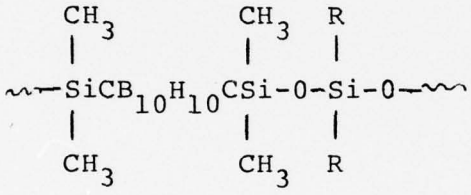

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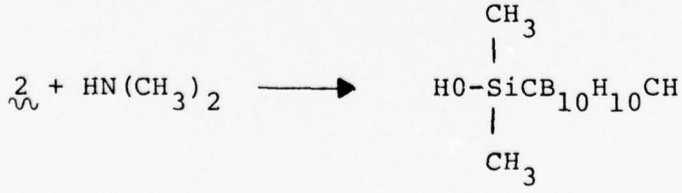
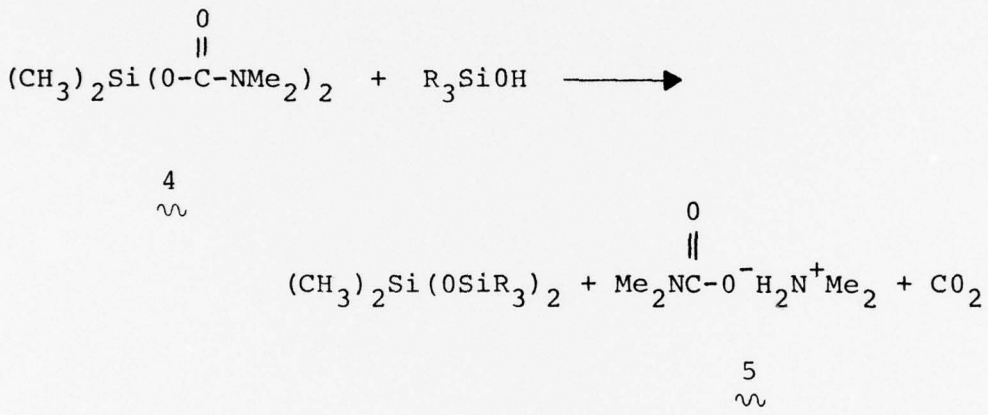
Our initial choice of 3 was bis(N,N-dimethylamino)-dimethylsilane (i.e., R,R = CH_3; X,X = $N(CH_3)_2$). We found that linear D_2-polymers were readily obtained under mild reaction conditions which had degrees of polymerization up to 50 ($\bar{M}_w$ 18,000). However attempts to achieve higher molecular weight were thwarted by a dimethylamine induced cleavage of the carborane-silicon bond in monomer 2.



Silyl carbamates have a relatively non-nucleophilic leaving group. Bis(N,N'-dimethylcarbamato)dimethylsilane, 4,

had high reactivity towards silanols. Moreover, at mild reaction conditions the carbamate leaving group was stable to decarboxylation presumably due to the formation of the carbamic acid salt, 5. Thus, the high reactivity of silyl carbamates coupled with the possible lack of deterious amine byproduct suggested their use as comonomers.

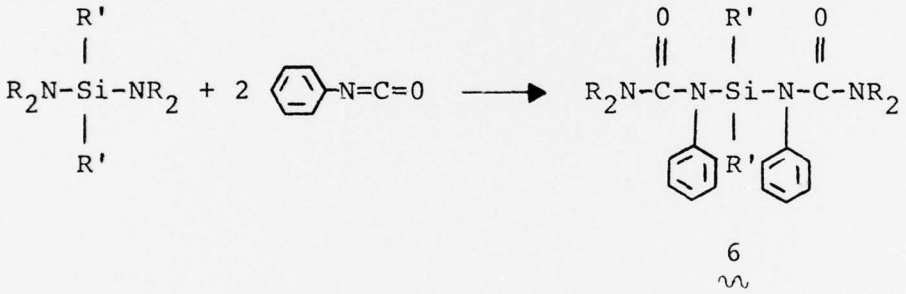


A variety of reaction conditions were tested with 2 and 4: (a) chlorobenzene solvent at room temperature; (b) chlorobenzene solvent at 4° under vacuum; (c) heptane solvent; (d) neat reagents at 40°. In all cases only low molecular weight materials were obtained. The limited molecular weights probably resulted from dimethylamine cleavage reactions. Apparently the carbamic acid salt 5 was not as stable as initially anticipated and decomposed into dimethylamine and CO_2 readily. Dimethylamine, on the basis of previous results, could limit molcular weights by inducing carborane-

silicon bond cleavage and, consequently, the formation of monofunctional chain terminating carborane-monosilanol.

Although we believed that further work could lead to better control of silyl carbamate polymerizations, we curtailed further experiments with these materials in order to turn our attention to bis-ureidosilane comonomers.

Bis-ureidosilanes, 6, were readily prepared by the rapid insertion reaction of isocyanates into the silicon-nitrogen bond of silyl amines. Although many structural



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examples had been cited, their utilization to form polymeric systems had not been reported with the exception of their use as room-temperature-vulcanizing agents for silanol terminated silicones.[6] We were particularly attracted to bis-ureidosilanes since the leaving group resulting from their reaction with carborane-disilanol 2 would be a neutral, unreactive urea.

Indeed, the condensation reaction of 6 and 2 proved to be most effective and provided high molecular weight (M_w $\geq$250,000) linear polymers. Moreover, this system allowed for a wide range of polymer backbone structural modifications.

Thus diphenyl, methylphenyl, and methylvinylsiloxanes could be incorporated into the polymer in order to improve performance and curing properties.

EXPERIMENTAL

Synthesis of Monomers

Bis(N-phenyl-N'-tetramethyleneureido)-dimethylsilane

Reagents:

n-Butyl lithium - 10 moles, Ventron, 2.4 M in hexane

Ethyl ether - 11 liters, anhydrous grade refluxed over K/Na alloy with about 2 g/l of benzophenone until mixture turns dark blue, then distilled under nitrogen.

Dichlorodimethylsilane - 600 ml, simple distillation under nitrogen b.p. 70°C.

Phenyl isocyanate - about 1 liter, vacuum distillation b.p. 85°C @ 57mm.

Pyrrolidine - 835 ml, relfuxed 16 hours over KOH and then distilled under nitrogen b.p. 88°C.

A 12 liter three-necked flask was equipped with a mechanical stirrer, dry ice condenser, nitrogen atmosphere and stopper. The equipemnt was assembled hot from oven and cooled under nitrogen purge.

Ten bottles (1 mole each) of butyl lithium in hexane were added to the reaction flask under nitrogen purge, followed by 5 liters of dry ether. A dropping funnel containing 835 ml (10 moles) of pyrrolidine was attached to the 12 liter flask and the dry ice trap was filled. The pyrrolidine was added over a period of 4 hours resulting in a milky white mixture. The heat of reaction caused the mixture to reflux gently during the addition. The mixture was allowed to stir for one hour after the addition was complete.

Under nitrogen purge the empty dropping funnel was replaced with another containing 600 ml of dichlorodimethylsilane (calc. 5.0 moles). Initial addition of the dichlorodimethylsilane was highly exothermic and was done extremely slowly. The reaction moderated as time progressed and the addition rate could be increased. The dichlorodimethylsilane was added over 4 hours. The mixture was left stirring for a period of at least twelve hours.

Filtration was accomplished through the sintered glass apparatus. The nitrogen purge was quite rapid and the opening at the top of the filtration funnel was shielded with aluminum foil to prevent moisture contamination. The initial filtrate came through cloudy and was washed with 1 liter of dry ether. The filtrate was yellow and slightly cloudy.

The filtrate was then concentrated by distillation. A three-necked 2 liter flask was equipped with a magnetic stirrer, distillation head, and a dropping funnel. As solvent was distilled off until the rate decreased to a slow dropwise distillation. The dropping funnel was then removed, a vacuum distillation head was attached and the mixture was then vacuum distilled. The main cut of bis(1-pyrrolidinyl)-dimethylsilane was collected in a tared 1 liter dropping funnel. b.p. 117 @ 24 mm, yield 829.2g calc. 84%.

A 12 liter flask with a mechanical stirrer, nitrogen inlet and stopper was assembled hot from the oven under nitrogen purge. A dropping funnel containing the 829.2g of bis-(1-pyrrolidinyl)-dimethylsilane was attached to the flask in place of the stopper and was added to the flask followed by 4 liters of dry ether. A funnel containing 931 ml of phenyl isocyanate was then attached and added slowly to the stirring solution. A small exotherm was produced. The addition was completed in 1 1/2 hours to yield a colorless solution. After stirring overnight, this solution usually produced a heavy white precipitate. In some instances precipitation did not occur and was facilitated by seeding with some authentic product.

The mixture was transferred via polyethylene tubing and under nitrogen. A total of 1 liter of dry ether was used for several rinsings of the reaction flask and washing the

filter cake. The filtration funnel was then stoppered. The flask containing the filtrate was removed and the filtrate was discarded. A small flask replaced the filtrate flask and the product was pumped on for two days.

After two days of pumping the funnel containing the product was brought into a dry box with bottles, spatulas, and other necessary equipment. The product and equipment were pumped on overnight in the dry box. The dry box was then filled with argon and the product was transferred to the tared bottles. Net yield of bis(N-phenyl-N'-tetramethylene-ureido)-dimethylsilane was 1569.5g. Yield from dichlorodi-methylsilane was 72%.

Bis(N-phenyl-N'-tetramethyleneureido)-methylphenylsilane

The procedure used was essentially the same as that given above except for the replacement of dichlorodimethyl-silane with dichloromethylphenylsilane. The bis(1-pyrrolidinyl)-methylphenylsilane product had a boiling point of 121°C at full pump (manifold pressure of 70 microns). The yield was 90%. The overall yield of bis(N-phenyl-N'-tetramethyleneureido)-methylphenylsilane was 79%

Bis(N-phenyl-N'-tetramethyleneureido)-diphenylsilane

In like manner the title compound was prepared in an overall yield of 57%. The bis(1-pyrrolidinyl)-diphenylsilane was prepared in 70% yield (b.p. 216/3 mm).

Bis(N-phenyl-N'-tetramethyleneureido)-methylvinylsilane

The bis(1-pyrrolidinyl)-methylvinylsilane intermediate had a b.p. of 117°C/16 mm (74% yield). By reaction with phenyl isocyanate, the corresponding bisureidosilane was prepared in a 62% overall yield.

1,7-bis(hydroxydimethylsilyl)-m-carborane

The meta-carborane-disilanol preparation was adapted from a literature procedure.[7]

Synthesis of Polymers

Under nitrogen in a flame dried, 250 ml three-necked round bottom flask equipped with a mechanical stirrer was placed a mixture of 19.88g (45.54 mmole) of bis(N-phenyl-N'-tetramethylene-ureido)-dimethylsilane, 14.77g (26.34 mmole) of bis(N-phenyl-N'-tetramethyleneureido)-diphenylsilane, and 1.455 (3.24 mmole) of bis(N-phenyl-N'-tetramethyleneureido)-methylvinylsilane. Dry chlorobenzene (25 ml) was added and after stirring for 30 minutes the reaction mixture was cooled to 0-10°C. The carborane disilanol was slowly added (via a solid addition tube) over a three hour period while maintaining the reaction temperature at -10° $\pm$ 5°C. The mixture was stirred moderately for 15 minutes at -10°C then allowed to warm slowly to room temperature and stirred overnight.

NMR spectroscopy was used to monitor the reaction stoichiometry, adjusting for side reactions and monomer impurities. Subsequent monomer additions were made slowly as chlorobenzene solutions via a syringe pump. Upon completion of the reaction, the mixture was filtered to remove the insoluble urea byproduct and then coagulated in methanol. After further washing with methanol, the polymer was dried at 150°C at 1-2 mm overnight. After drying 28.09g of polymer (91.2% yield) was obtained.

Molecular Weight Determination

Molecular weights and molecular weight distributions (dispersity) were determined by gel permeation chromatography for a series of D_2-m-carborane-siloxane polymers. The molecular weight distributions ($\bar{M}_w/\bar{M}_n$) were broad and usually low molecular weight tails are present. The $\bar{M}_w/\bar{M}_n$ value of 3.3 to 4.0 were common.

The relative viscosities in chloroform at 25°C for a series of methylphenylsiloxane modified D_2-carborane-siloxanes can be correlated with the weight average molecular weight by the semi-empirical Mark-Houwink equation.[8]

$$\eta = KM^a$$

For this system a is 0.72 and K is 1.02×10^{-4} (correlation coefficient 0.999).

RESULTS AND DISCUSSION

In early experiments the reactivity of ureidosilanes in polymerization reactions was established by carrying out experiments wherein they were prepared from a silyl amine and an isocyanate in the polymerization solvent and then directly combined with carborane disilanol without prior isolation or purification. However, only low molecular weight products were isolated and it was concluded that optimization of the polymerization reaction could best be achieved by using pre-synthesized bis-ureidosilane.

Polymerizations in the absence of solvents in which a mixture of bis-ureidosilanes and a slight stoichiometric deficiency of carborane-disilanol were heated to 160°C (112 minutes) and then maintained at 160-170°C for two hours resulted in a reproducible molecular weight of 18,000. An examination of the effect of reaction stoichiometry on molecular weight indicated the occurance of one or more side reactions. Nevertheless, the molecular weights obtained were considerably higher than those previously reported.[4]

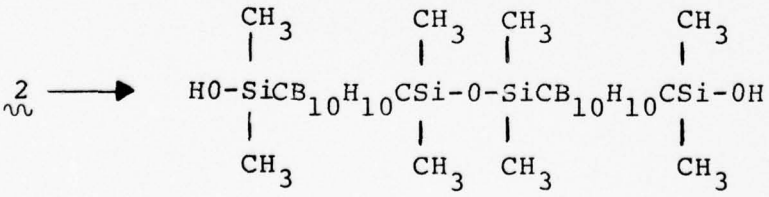
These initial results with bis-ureidosilanes were sufficiently encouraging to warrant more detailed research. This involved determination of the purity and stability of the comonomers and end-group analysis of the polymer. For the latter we developed a particularly useful technique in

which the polymer end-groups were monitored during the course of a polymerization using 100 MH_z H^1 nmr. This approach proved to be the key to obtaining the required high molecular weights and should have broad utility in condensation polymer chemistry.

Purity and Stability of Monomers

The purity of m-carborane-disilanol, 2, was established by mp, nmr, and glpc characterization. The latter approach involved silylation of silanol groups using commercial BSA reagent (bis-silyl acetamide). The results indicated a purity of ≥99.5% which should be sufficient for obtaining high molecular weight polymers.

Carborane-disilanol was not stable towards self-condensation at elevated temperatures. When neat 2 was heated at 160° for 18 hours we found evidence by nmr for self-condensation at least to the dimer stage 7.



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This self-condensation reactions must have been an important

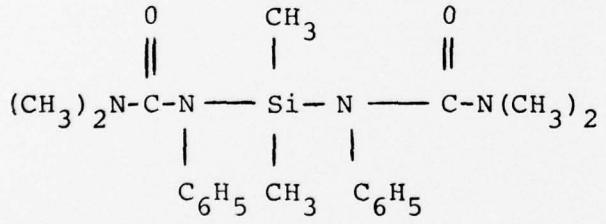
source of difficulty in the high temperature polymerization experiments described above and may actually be enhanced in the polymerization medium. This reaction was less important at lower temperatures and in solvents. For example, in dichloroethane solvent at room temperature no self-condensation was observed over a 24 hour period. The same result was obtained in the presence of phenylurea (a by-product of the polymerization reaction) and large amounts of phenyl isocyanate (a potential dehydration catalyst). However, about 10% self-condensation was observed in the presence of phenyl isocyanate after 7 days at room temperature. No evidence for other possible decomposition reactions such as carborane-silicon bond cleavage was observed.

From these results we concluded that polymerizations are best carried out in solvents preferably at reduced temperature. Under these reaction conditions there should be essentially no molecular-weight limiting side reactions involving the m-carborane-disilanol.

The high reactivity of ureidosilanes with ambient moisture suggested the use of nmr as the most convenient approach for determining monomer purity. Moreover, nmr was used to monitor the reaction of phenyl isocyanate and silyl diamine. Thus, it was confirmed that purer ureidosilane could be obtained if the reaction temperature and rate of addition of phenyl isocyanate were carefully controlled.

Fast addition rates and higher reaction temperatures tended to favor formation of mono- and di-biurets. Interestingly, the mono-biuret tended to disproportionate on standing in solution. Most important, nmr determination of the amount of impurities in a particular ureidosilane sample allowed a more precise selection of initial polymerization reaction stoichiometries.

Early polymerization studies were carried out using bis(N,N-dimethyl-N'-phenylureido)dimethylsilane (8). However, nmr analysis revealed numerous impurities such as N,N-dimethyl-N-phenylurea (9), the mono-biuret (10) which is obtained from the insertion of phenyl isocyanate into the silicon-urea bond of bis-ureidosilane. Barely detectable amounts of dibiuret (11) were also observed.



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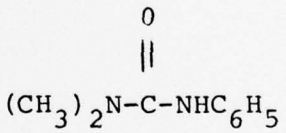

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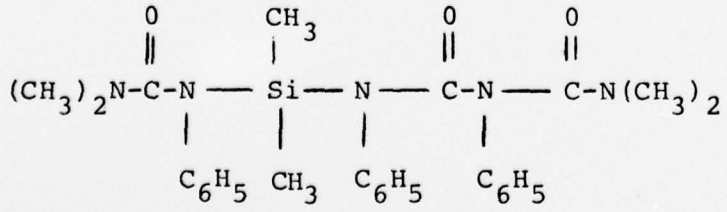

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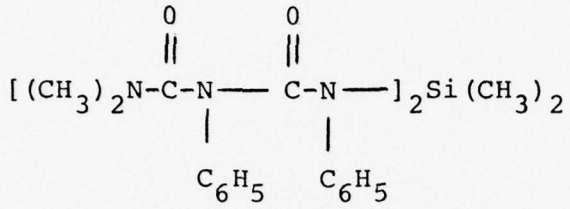

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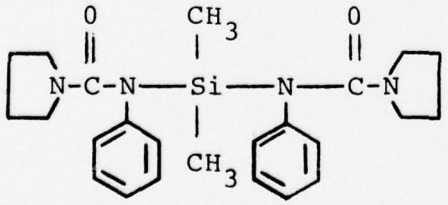
Clearly, an important problem was the difficulty in handling the purifying 8. This material was generally obtained as a viscous oil which slowly crystallized. Impurities were considerable and could only be removed by a cumbersome molecular distillation technique. In contrast, the bis-ureidosilane 12 was an easily handled solid which could be purified by crystallization from ether. Even though the urea 13 was always an impurity, it could be readily determined and otherwise did not appear to affect the polymerization reaction.



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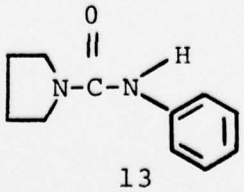

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After determining the inherent impurities the thermal stability of several ureidosilane samples were examined. Neat ureidosilane did not decompose after heating at 160° for 18 hours. However, we did observe generation of phenyl isocyanate and mono-ureidosilane after heating at 160° *in vacuo*. Bis-ureidosilanes were found to be completely stable in dichloroethane solvent at room temperature.

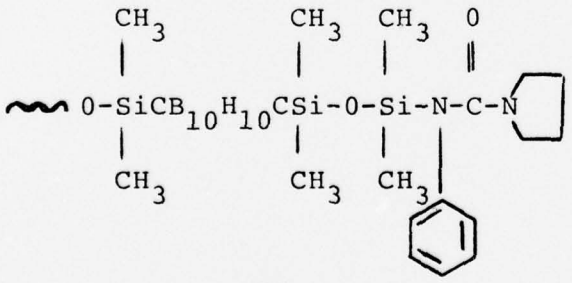
Monitoring the Polymerization Reaction by NMR

The successful use of nmr to determine purity and stability of the bis-ureidosilanes and carborane-disilanol monomers led to nmr monitoring of the polymerization reaction itself. This has turned out to be a particularly productive approach which has allowed us to obtain for the first time the high molecular weights required for useful elastomeric properties.

The polymerization reaction was extremely rapid. For example, when a fractional equivalent of bis-ureidosilane was added to a solution of carborane-disilanol in deuterochloroform at room temperature, an immediate nmr scan showed that all of the ureidosilane was consumed. This high reaction rate at mild conditions and without catalysts was particularly significant since it allowed considerable flexibility in choosing reaction conditions.

The second important result was that the extent of polymerization and the polymer end groups could be monitored. The extent of polymerization could be measured quantitatively by monitoring the appearance of resonances due to urea by-product, $Si-CH_3$ proton resonances for the silanol comonomer. In addition, during the course of the polymerization the $Si-CH_3$ proton resonance of the growing polymer was observed. These are a complex set of signals for lower-molecular weight oligomers; as the polymer grows these simplify to give only two signals in the ratio 1:2 as shown in Figure 1.

A third significant result was that the polymer end groups could be monitored. It was possible to determine 0.25% of the urea type end group, 14, by monitoring the designated resonances. Silanol end groups could be monitored only to the 2% level owing the interference with signals due to the polymer (Figure 1).



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A procedure for optimizing the polymer molecular weight has emerged from the above experiments. The purity of the particular batch of bis-ureidosilane monomer was

determined by nmr. A near stoichiometric amount of carborane disilanol was then slowly added at -10° to minimize the reaction exotherm. At the completion of the addition nmr was again used to determine the nature and amount of reactive end-groups. The required amount of additional co-monomer was then added. This is exemplified in Figure 2. The nmr of the reaction mixture indicated an excess of bis-ureidosilane and ureidosilane end groups on the polymer. Thus a deficiency of carborane disilanol existed. Additional carborane disilanol reacted with the bis-ureidosilane and ureidosilane end groups and resulted in an increase in the molecular weight to 200,000. In general, molecular weights >200,000 can now be routinely obtained.

Versatility of Polymerization Reaction

The use of bis-ureidosilane monomers has resulted in the preparation of high molecular weight linear polymers. The effect of molecular weight on the mechanical properties is shown is Table I. A "quantum jump" in elongation occurs as the molecular weight is increased from 150,000 to 283,000. Improvements in tensile strength are also noted. Similar increases in properties was noted in vulcanizates prepared from these materials.[9]

Because of the mild reaction conditions in the condensation of carborane disilanol with bis-ureidosilanes, structural

modification of the polymer backbone can be readily achieved. For example, through the use of various combinations of dimethyl and diphenyl- or methylphenyl-bis-ureidosilanes amorphous polymers were obtainable.[10] This increased phenyl content improved the thermo oxidative stability of the polymer.[9, 10] Methyltrifluoropropyl groups can similarly be incorporated to improve the solvent resistance.[11] To facilitate vulcanization, methylvinylsiloxane moieties was readily incorporated into the polymer backbone. Thus elastomers with useful general properties after heat aging in air at 315°C for 300 hours were produced.[9, 12]

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FIGURE 1.

NMR of Polymerization Reaction

FIGURE 1.

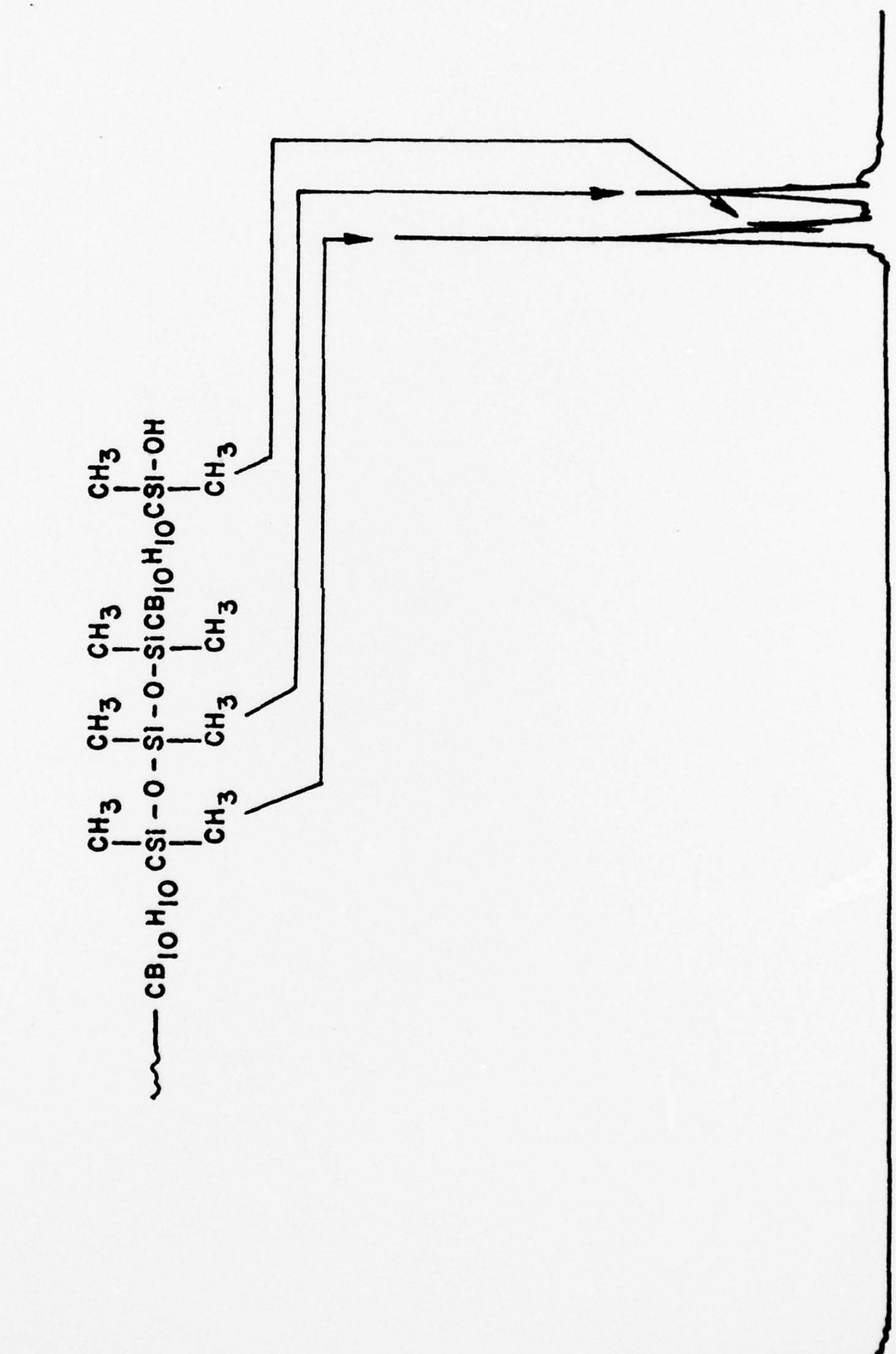
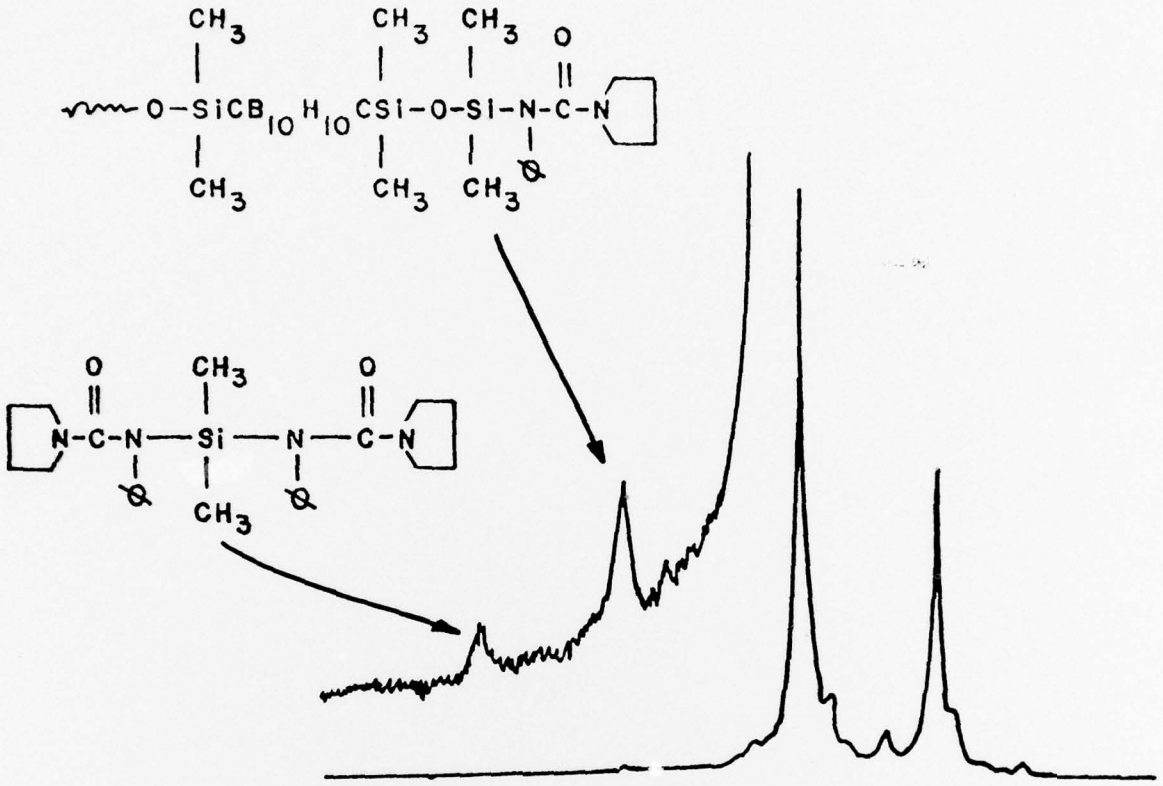


FIGURE 2.

NMR Technique Used to Adjust Stoichiometry

FIGURE 2.

REACTION MIXTURE



AFTER ADJUSTMENT

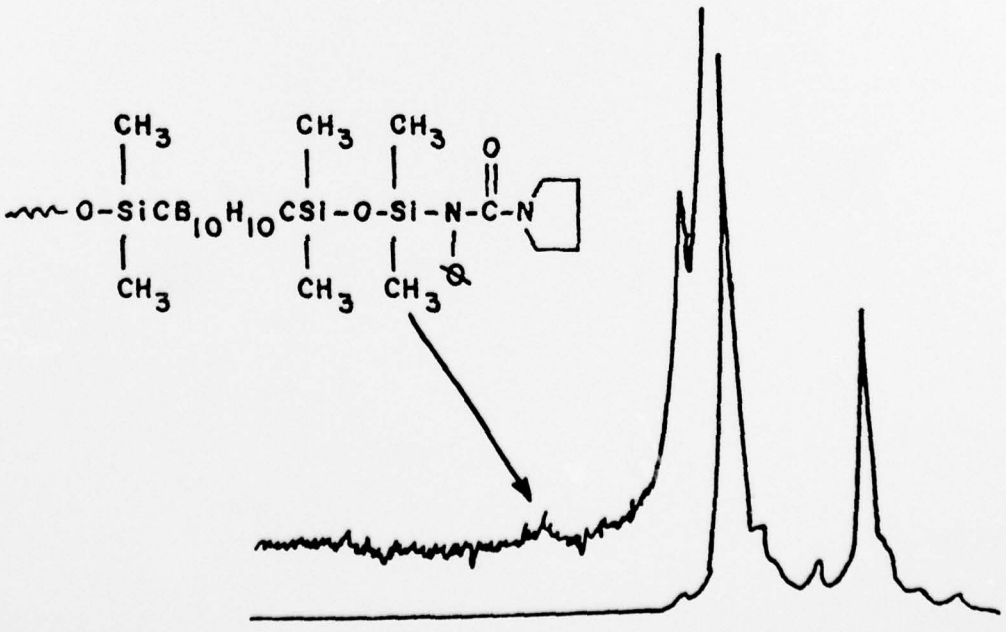


TABLE I

Mechanical Properties as a
Function of Molecular Weight*

Mw	Young's Modulus, psi	Tensile Strength, psi	Elongation at Break, %
50,000	2950	100	5
150,000	2900	103	60
283,000	3300	333	700

* Properties measure at 25.0°C for D_2-m-carborane-dimethyl/diphenyl-siloxane (67/33 mole %).