Rheovibron (Model DDV-II): Samples were cut into narrow strips aproximately 3 cm in length, 0.3 cm in width, and 0.002 cm in thickness. Runs were made at a frequency of 35 Hz at a heating rate of 5 °C/min in an inert atmosphere. The dynamic moduli of films were calculated using the following equation:

$$|E^*| = \frac{2}{(A)(\mathrm{DF} - K)} \frac{L}{S} \times 10^9 \ \mathrm{dyn/cm^2}$$

where A is a constant given by the instrument manual,[10] DF is the value of the dynamic force dial when measuring tan δ, L is the length of the sample, S is the cross-sectional area in cm^2, and K is an error constant due to the displacement of the stress gauge. Values of the dynamic storage modulus E' were obtained as follows: $E' = |E^*| \cos \delta$.

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D_2-*m*-Carborane Siloxanes. 7. Synthesis and Properties of Ultra-High Molecular Weight Polymer

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ABSTRACT: A new two-step synthesis of linear, ultra-high molecular weight D_2-*m*-dodecacarborane siloxane was developed based on the preparation of a carborane silanol terminated prepolymer which was subsequently advanced in molecular weight to $>10^6$. This was the result in part of an improved synthesis for the bis(ureido)silane monomers of >98% purity and the development of a reverse addition heterophase polymerization technique. The ultra-high molecular weight polymers exhibited improved thermal mechanical properties as a result of increased chain entanglement of the polymer chains. Superior thermal stability in air was exhibited up to 800 °C.

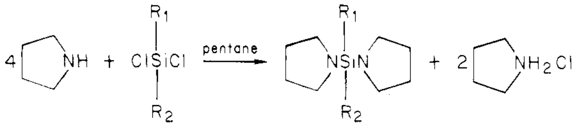
Recently we described the synthesis of linear, high molecular weight D_2-*m*-carborane siloxanes based on the condensation reaction between bis(ureido)silanes and carborane disilanol.[1-3] These polymers have unusual thermal stability and have potential utility as high-temperature elastomers.[1,4,5]

In previous work, polymers with molecular weights up to 250 000 were prepared.[1-3] Within the range of 50 000 to 250 000, an increase in the molecular weight of the polymer resulted in improvements in the mechanical properties for both polymer and vulcanizates.[4] Similar improvements in properties with increasing molecular weight were noted for poly(dimethylsiloxane).[6] Thus, a rapid improvement in the tensile strength was noted for poly(dimethylsiloxane) with increasing molecular weight up to 500 000.[6] Therefore, further advances in the molecular weight of D_2-*m*-carborane siloxane were desirable.

This paper describes the development of a synthetic route to ultra-high molecular weight ($>10^6$) D_2-*m*-carborane siloxane polymers[7] and the evaluation of their unique properties. In addition, this paper describes the improved synthesis of bis(ureido)silane monomers and the techniques used for the synthesis of consistantly high molecular weight carborane siloxane polymers using these monomers.

Experimental Section

Synthesis of Monomers. The bis(amino)silane intermediates used for the synthesis of bis(ureido)silanes were originally prepared using *n*-butyllithium to deprotonate the appropriate amine.[3] An improved synthesis was developed which involved the direct reaction of 4 equiv of amine with a dichlorosilane.



(1)

The preparation of a bis(pyrrolidinyl)silane is described below:

Bis(pyrrolidinyl)dimethylsilane. A three-necked, 2000-mL flask was equipped with a mechanical stirrer, a reflux condenser, a nitrogen inlet, and an addition funnel. Dichlorodimethylsilane (129 g, 1 mol) and heptane (200 mL) were placed in the reaction vessel. Pyrrolidine (284.5 g, 4 mol) was added dropwise over a period of 2 h with stirring and cooling in an ice bath. The reaction was slightly exothermic, and solid amine hydrochloride began to separate immediately.

After completion of the addition, the cooling bath was removed and the reaction mixture was stirred at ambient temperature for 12 h. The solid was removed by filtration under nitrogen and washed with three 50-mL portions of heptane. The solvent was removed by distillation through a 12-in Vigreaux column at atmospheric pressure under nitrogen. Distillation of the residue gave 174 g (87 percent) of bis(pyrrolidinyl)dimethylsilane, bp 59–60 °C (0.025 mm).

Bis(pyrrolidinyl)methylphenylsilane was prepared in a similar manner in 92% yield, bp 114–8 °C (0.05 mm).

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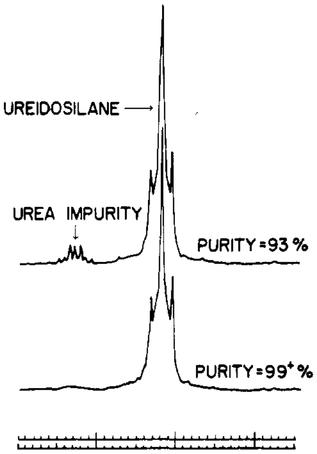
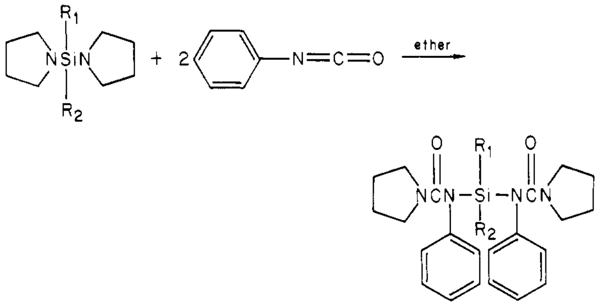


Figure 1. NMR spectra (100 MHz) of the methylene protons on the pyrrolidino group in ureidosilanes and the urea impurity.

Bis(ureido)silanes were conveniently prepared by the reaction of a bis(amino)silane with 2 equiv of phenyl isocyanate in ether.



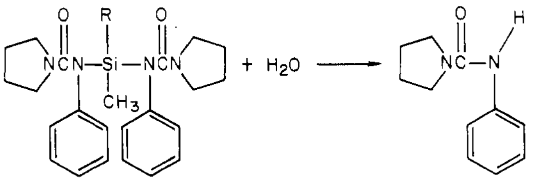
(2)

Their preparation is described below:

Bis(*N*-phenyl-*N*′-pyrrolidinyl)dimethylsilane. A 2000-mL, three-necked flask was equipped with a magnetic stirrer, a nitrogen inlet, and an addition funnel. Bis(pyrrolidinyl)dimethylsilane (100 g, 0.5 mol) and 400 mL of anhydrous ether were placed in the flask. The reaction mixture was cooled to 0–5 °C in an ice bath. Phenyl isocyanate (119 g, 1 mol) was transferred to the addition funnel by syringe and added dropwise over a period of 1 h. The solid product slowly separated during the addition. Stirring was continued for 1 h after completion of addition and then stopped to allow the solid product to settle out. The ether was decanted under nitrogen and replaced by 400 mL of pentane. The pentane layer was decanted after being stirred for 15 min. This procedure was repeated with two additional 400-mL portions of pentane. Drying in vacuo gave the product: 199 g (91%); mp 124–125 °C.

Bis(*N*-phenyl-*N*′-pyrrolidinyl)methylphenylsilane was prepared in a like manner in 80% yield, mp 98–101 °C.

NMR Analysis of Ureidosilanes. The high reactivity of ureidosilanes with ambient moisture suggested the use of NMR as the most convenient method for determining monomer purity. The NMR analysis revealed that the substituted urea formed from the hydrolysis of the ureidosilanes (eq 3) could be identified by the addition of a known quantity of an authentic sample of the compound. The methylene protons of the pyrrolidine substituent group on the ureidosilanes and the substituted urea were readily identifiable as shown in Figure 1. The substituted urea content was used as the criteria for purity of the ureidosilane monomers.



(3)

A representative spectra for the determination of the purity of ureidosilanes prepared via the lithio amine[1,3] is shown in Figure 1. The purity of this material ranged from 92 to 98 wt %. The purity of the ureidosilanes prepared by the method described in this article was routinely greater than 99 wt % as shown in the NMR spectra in Figure 1.

Synthesis of Polymers. Ultra-high molecular weight D_2-*m*-carborane siloxane was prepared by a two-step synthesis. Initially, a carborane silanol terminated carborane siloxane prepolymer was synthesized, isolated, and characterized. This prepolymer was then advanced in molecular weight by the addition of a predetermined amount of bis(ureido)silane which coupled the silanol terminated prepolymer.

The experimental procedure for the synthesis of these polymers is described below:

Carborane Silanol Terminated Carborane Siloxane Prepolymer. A 250-mL, three-neck flask was equipped with a mechanical stirrer, a nitrogen inlet, and a 100-mL, one-neck satellite flask. Carborane disilanol (28.3 g, 0.097 mol) was weighed into the 250-mL flask. Bis(ureido)methylphenylsilane (14.3 g, 0.029 mol) and bis(ureido)dimethylsilane (25.1 g, 0.057 mol) were weighed into the 100-mL satellite flask under nitrogen. The flask containing the mixed bis(ureido)silanes was connected to the 250-mL flask with a flexible solids addition tube. Dried chlorobenzene (28 mL) was added to the carborane disilanol and the slurry was stirred and cooled to −10 ± 5 °C. A portion-wise addition of the solid bis(ureido)silanes was conducted over 4 h. At the conclusion of the addition period, 1 mL of chlorobenzene was syringed into the reaction flask to wash the remaining solids into the reaction mass. The reaction was cooled for an additional 1.5 h at −10 ± 5 °C followed by additional cooling of the reaction flask in an ice bath. The reaction was then allowed to warm up to ambient temperature overnight.

The carborane siloxane reaction mass was diluted with chlorobenzene and filtered to remove the solid reaction byproduct. The carborane siloxane/chlorobenzene solution was precipitated three times from a large volume of methanol or acetonitrile. The precipitated polymer was then vacuum pumped to remove retained solvents. The recovered polymer weighed 27.2 g (85.6%), reduced viscosity (RV) = 0.53 dL/g in $CHCl_3$ at 25 °C.

Ultra-High Molecular Weight D_2-*m*-Carborane Siloxane. A 100-mL, one-neck flask was equipped with a magnetic stirring bar and a nitrogen inlet. Carborane siloxane polymer (5.0 g, 1.1×10^{-4} mol) was weighed into the flask, and the flask was vacuum pumped at 100 °C overnight to dry the sample. The flask was septum sealed under nitrogen and cooled; 25 mL of dry chlorobenzene was added by syringe. The flask was shaken to dissolve the polymer prior to being placed over a magnetic stirrer. The polymer solution was slowly stirred under a nitrogen blanket. Bis(ureido)methylphenylsilane (0.19 g, 3.77×10^{-4} mol) in 2.0 mL of dry chlorobenzene was slowly titrated into the polymer solution until the polymer solution became extremely viscous. The polymer mass was then back titrated with carborane disilanol (0.04 g, 1.4×10^{-4} mol) in 20 mL of chlorobenzene over 5.0 h. The carborane siloxane polymer was diluted with 30 mL of chlorobenzene and poured into 500 mL of methylene chloride to lower the viscosity of the polymer solution. The polymer was precipitated from 3 L of methanol and vacuum dried at 100 °C. The recovered ultra-high molecular weight polymer weighed 4.7 g (94.0%), RV = 5.12 dL/g in $CHCl_3$ at 25 °C.

Polymer Characterization. Thermogravimetric data were obtained on a Perkin-Elmer TGS-1 with a heating rate of 10 °C/min. The heat of fusion data were obtained on a Perkin-Elmer DSC-2 with a heating rate of 10 °C/min. Gel-permeation chromatography data were obtained on a Water's Instrument, Model 200, using THF at 30 °C. Five columns, in series, were used with porosities of 1.5×10^6, 1.5×10^5, 2×10^4, 1.5×10^4, and 60 Å, respectively. Mechanical property data were obtained on a Instron Tensile Tester, Model 1122, at 2 in./min for the stress–strain data and at 0.2 in./min for the modulus data.

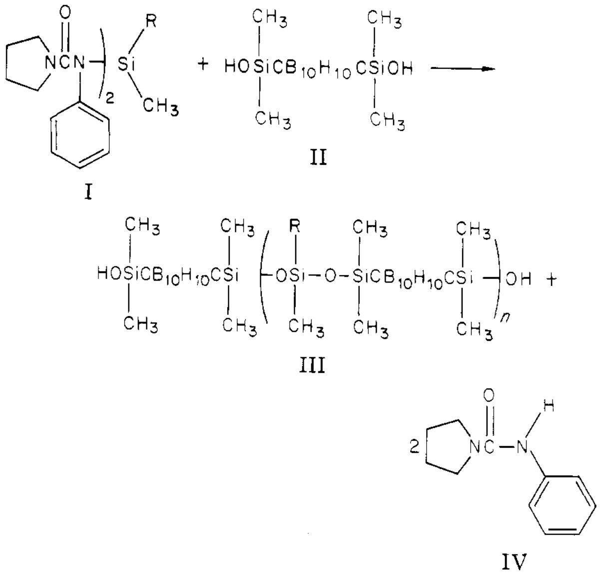
Results and Discussion

A significant synthetic advance was made which allowed the preparation of bis(ureido)silane monomers in greater than 98% estimated purity. This can be compared with the same monomers which were previously prepared in only 85–8% purity. Thus, high-purity monomers were available on a routine basis for use in the preparation of carborane siloxane polymers.

Our earlier polymer work resulted in the preparation of D_2-*m*-carborane siloxane polymers with molecular weights of approximately 200 000.[1-3] Preparation of carborane siloxane polymers by the addition of carborane disilanol to the bis(ureido)silane monomers resulted in polymers of unpredictable molecular weights. Monitoring the polymerizations by NMR and subsequent titration with the reaction monomers resulted in increased polymer molecular weights in a majority of the reactions. However, attempts to prepare polymers of consistant molecular weight, or with molecular weights greater than 300 000, were unsuccessful.[1-3]

Consistantly high molecular weight polymers were prepared by the reverse addition of bis(ureido)silanes to carborane disilanol in chlorobenzene. This reverse addition technique also resulted in the preparation of carborane disilanol terminated carborane siloxane polymers. A portion of the polymers prepared by this reverse addition technique were isolated in a manner that allowed them to be subsequently advanced to ultra-high molecular weight by reaction with bis(ureido)silane monomer. Thus, a two-step synthesis was achieved using the high-purity monomers that resulted in D_2-*m*-carborane siloxane polymers with molecular weights of up to 5 000 000.

Polymer Preparation. Carborane silanol terminated D_2-*m*-carborane siloxane prepolymer, III, was prepared by the reverse addition of bis(ureido)silanes [I, R = CH_3, C_6H_5 (2:1)] to an excess of carborane disilanol, II, in chlorobenzene (or toluene) as shown in eq 4.



(4)

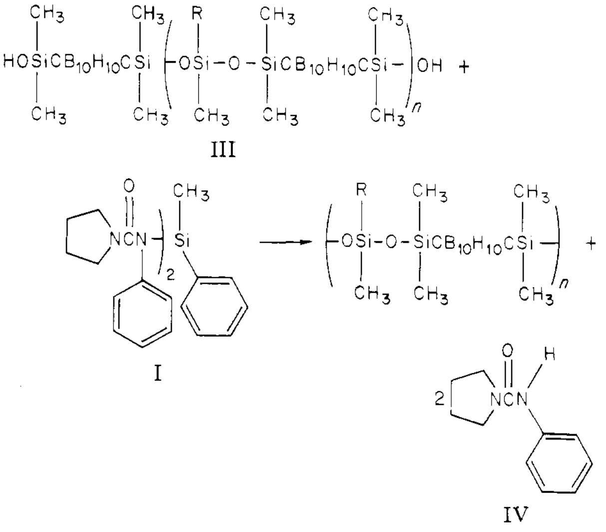
In two similar reverse addition reactions, an excess of 6 and 12 mol % of carborane disilanol was present in the chlorobenzene at -10 ± 5 °C. Theoretically, the use of a 6 mol % excess of carborane disilanol would result in a carborane silanol terminated D_2-*m*-carborane siloxane, III, with a molecular weight of about 25 000, and a 12 mol % excess would result in lower molecular weight prepolymer. However, both polymers exhibited considerably higher, and equivalent, molecular weights, $\bar{M}_w = \sim 150\,000$.

It is believed that these higher than expected molecular weights are achieved because the carborane disilanol is relatively insoluble at -10 ± 5 °C in chlorobenzene ($\sim$0.044 g/mL at 25 °C), and the polymerization is run with a minimum of chlorobenzene ($\sim$1 mL/g of carborane disilanol). Since the concentration of dissolved carborane disilanol was low during the addition of the solid bis(ureido)silane, the reaction stoichiometry was actually controlled by the rate at which the carborane disilanol transfers into the solution phase. Therefore, the dissolved bis(ureido)silanes were titrated by the dissolving carborane disilanol. The reaction stoichiometry was not controlled by the total amount of carborane disilanol but rather by its rate of dissolution into the heterophase reaction media. The excess carborane disilanol ultimately consumes the ureidosilane groups and leaves the prepolymer with carborane silanol end groups.

Active hydrogen analysis of the $-Si(CH_3)_2OH$ end group functionality gave a value of 750 ± 30 ppm for –OH content which calculates to a number average molecular weight ($\bar{M}_n$) of 45 310 and a degree of polymerization (DP) of $\sim$122. The carborane siloxane prepolymer must be highly purified to avoid destruction of the terminal silanol groups. Trace quantities of amine present via the urea byproduct, IV, were shown to cleave the silanol end groups.[3] A convenient and reliable isolation and purification technique was not defined for the carborane siloxane prepolymers.

Only a portion of the prepolymer samples synthesized were subsequently advanceable to ultra-high molecular weight polymer. When a sample of carborane silanol terminated prepolymer was obtained that would advance in molecular weight, multiple advancement reactions were successfully performed with the sample. The cause of the nonadvanceability of many of the prepolymer samples was not defined. Whether this lack of reactivity was due to problems in the polymerization, in the isolation and purification techniques, or both was not satisfactorily resolved.

The molecular weight of the carborane silanol terminated polymer III was advanced in a subsequent reaction by a titration with bis(ureido)methylphenylsilane monomer, I, as shown in eq 5.



(5)

This resulted in the preparation of linear D_2-*m*-carborane siloxane polymers with molecular weight in excess of 10^6. Attempts to prepare ultra-high molecular weight D_2-*m*-carborane siloxanes by the in situ titration of the prepolymer were only partially successful.

Gel-Permeation Chromatography. Molecular weights and molecular weight distributions for D_2-*m*-carborane siloxane polymers were determined by gel-permeation chromatography. A comparison of the weight average molecular weights vs. the reduced viscosities of the polymers is detailed in Table I. The molecular weight distribution curves comparing low molecular weight and ultra-high molecular weight polymer are graphically shown in Figure 2. The molecular weight distribution of the

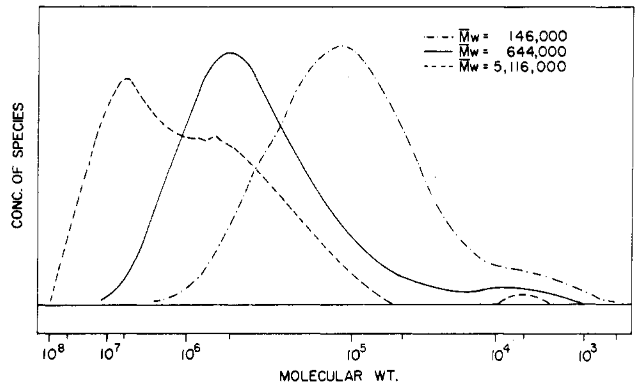


Figure 2. Gel-permeation chromatography of D_2-*m*-carborane siloxanes.

Table I
Molecular Weights of Uncured D_2-*m*-Carborane Siloxane Polymers

reduced viscosity,[a] dL/g	wt av mol wt ($\overline{M}_w$)
0.53	146 100
0.98	378 600
1.50	644 000
2.55	1 681 000
3.64	2 230 000
5.12	5 116 000

[a] Reduced viscosity in $CHCl_3$ at 25 °C.

ultra-high molecular weight polymer was nonuniform due to the extremely high viscosity of the polymer solution during the final stages of the coupling reaction. These high viscosities caused inefficient stirring and permitted the presence of unreacted low molecular weight oligomers.

Thermal Mechanical Properties. D_2-*m*-Carborane siloxane polymer was prepared over a wide range of molecular weights which allowed the determination of the ultimate mechanical properties achievable with this uncured polymer.[8] Mechanical properties were obtained on D_2-*m*-carborane siloxane polymers ranging in molecular weight from 146 100 up to 5 116 000. Significant increases in the tensile strength and elongation at break were exhibited when the molecular weight was increased to 644 000 and above. The melt flow and the melt failure were also affected by increasing molecular weight of the polymer. The polymers with molecular weights of 2 000 000 and above did not exhibit melt flow or melt failure when tested on the Instron at elevated temperatures. The mechanical properties of the D_2-*m*-carborane siloxane polymers as a function of their molecular weights are shown in Table II.

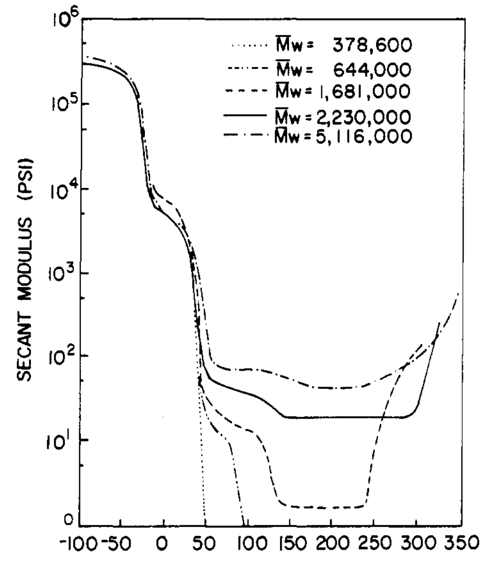


Figure 3. Comparative modulus vs. temperature of uncured D_2-*m*-carborane siloxanes.

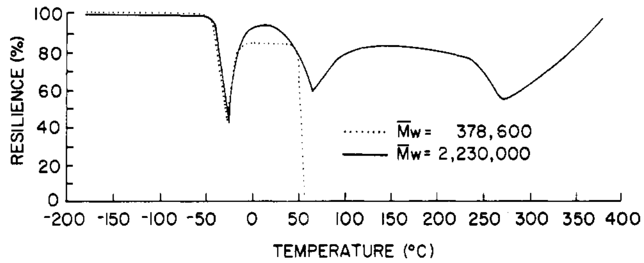


Figure 4. Resilience vs. temperature of uncured D_2-*m*-carborane siloxanes.

The carborane siloxane polymer samples were processable by compression molding with the exception of the highest molecular weight polymer which was solvent cast. Solvent casting had some effect on the mechanical properties, but the sample exhibited a good tensile strength, 680 psi, and high elongation at break, 600%. The uncured carborane siloxane polymers slowly crystallized upon standing for 2 to 4 days at ambient temperature.[10] The mechanical properties were obtained on polymer samples that were allowed to solidify for four or more days at ambient temperature.

The *E*/*T* curve (modulus vs. temperature) shown in Figure 3 graphically illustrates the effect of molecular weight on the modulus of the sample up to 300 °C. At temperatures below −30 °C, polymers are rigid and glassy with a high modulus. As the temperature increases, the polymer passes through the glass transition region, −27 °C, where flexibility appears. At ~50 °C, the polymer melts and a large decrease in the modulus is exhibited. The lower molecular weight polymers (378 600 and 644 000) exhibit melting and liquid flow at ~50–90 °C. However, the higher molecular weight polymers have sufficient chain entanglements to exhibit a rubbery transition region with further increases in the temperature of the sample. At these higher temperatures, the polymers reach a fairly constant rubbery plateau. The higher molecular weight

Table II
Mechanical Properties of Uncured D_2-*m*-Carborane Siloxane Polymer as a Function of Molecular Weight

reduced viscosity,[a] dL/g	0.53	0.98	1.50	2.55	3.64	5.12
mol wt[b] ($\overline{M}_w$)	146100	378600	644000	1681000	2230000	5116000
Young's modulus, psi	5300	4290	4100	3635	4700	2800
tensile strength, psi	192	251	750	752	695	680
elongation at break, %	20	30	410	300	450	600
yield strength, psi	none	163	290	193	207	106
yield elongation, %	none	30	13	25	15	20
melt flow, °C	~50	~50	~90	none	none	none
melt failure, °C	~90	~100	~190	none	none	none

[a] Reduced viscosity in $CHCl_3$ at 25 °C. [b] Molecular weight by GPC.

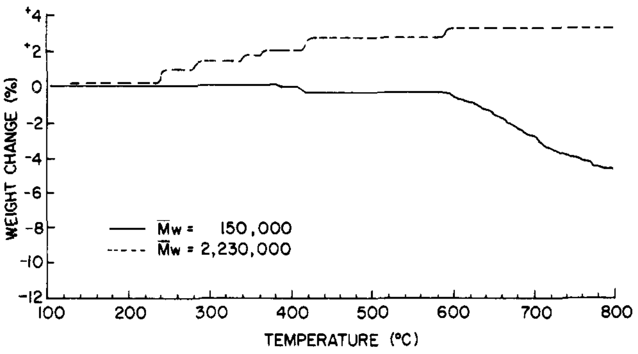


Figure 5. Thermogravimetry of D_2-*m*-carborane siloxanes in air.

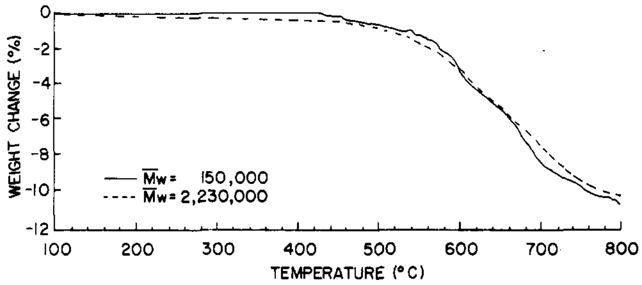


Figure 6. Thermogravimetry of D_2-*m*-carborane siloxanes in nitrogen.

polymers begin to oxidatively cross-link at ~240 °C which causes a significant increase of the modulus. The higher modulus plateau of the polymer sample with a molecular weight of 5 116 000 is due to the greater chain length and entanglement of the linear polymer.

Figure 4, which plots the polymeric resilience vs. temperature, shows the glass transition temperature (T_g) of −27 °C and the polymer melting temperature (T_m) of 53 °C. After the melting temperature, the higher molecular weight polymer, 2 230 000, fails to recover its resiliency until ~270 °C where the polymer begins to oxidatively cross-link. The lower molecular weight polymer, 378 600, melt flows and fails at 53 °C since the polymer chain is insufficiently long to effect chain entanglements.

Thermal Stability. The thermal stability of ultra-high molecular weight D_2-*m*-carborane siloxane polymer was determined by thermogravimetric analysis (TGA) up to 800 °C in air and nitrogen and compared to a sample with a low molecular weight. These data are shown in Figures 5 and 6. D_2-*m*-Carborane siloxane polymers were very heat stable in both air and nitrogen up to 600 °C. In fact, the ultra-high molecular weight polymer ($\bar{M}_w$ = 2 230 000) was very stable in air up to 800 °C as shown by the 4% weight gain of the test sample in Figure 5. Oxidative cross-linking, which is known to occur above 230 °C, more than compensates for any weight loss due to chain scission. The lower molecular weight polymer ($\bar{M}_w$ = 146 100) from which the higher molecular weight polymer was synthesized exhibits a 4% weight loss at 800 °C. The shorter polymer chains can produce volatile fragments more easily since fewer bonds need to be broken and oxidative cross-linking cannot compensate for the weight loss.

In nitrogen, the thermal stabilities of both the ultra-high and lower molecular polymers were very similar up to 800 °C, Figure 6. Both polymers began to lose weight at 400 °C, and the weight loss approaches 11% at 800 °C. In the absence of air, the polymers were degraded by chain scission.

Conclusions

The use of high-purity bis(ureido)silane monomers in the reverse addition polymerizations permitted the preparation of consistantly high molecular weight carborane siloxane polymers. In selected cases, carborane silanol terminated prepolymers were isolated from these reactions that were subsequently advanceable to ultra-high molecular weight. The ultra-high molecular weight carborane siloxane polymers exhibited improved thermal mechanical and thermal stability properties. This was due to increased chain entanglement of the polymer which began to have an increasing effect in the polymers with molecular weights above 1.6 × 10^6. Carborane siloxane polymers with molecular weights of 2 × 10^6 began to exhibit properties similar to vulcanizates prepared with earlier samples of low molecular weight polymer.

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(10) Crystalline dimethyl D_2-*m*-carborane siloxane polymers have a heat of fusion of 5–7 cal/g.[9] Methylphenyl modified (33 mol %) carborane siloxane polymers undergo a slow crystallization at ambient temperature. After 24 h, the heat of fusion is 0.05 cal/g, and after 7 days, a value of 2.4 cal/g is obtained. Vulcanization of these polymers eliminates this crystallization.