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Synthesis, Characterization, and Platinum-Catalyzed Hydrosilylation Cross-Linking of Unsaturated Si–H Carbosilanes: Random 2:1:1 and 2:$\sim$1:$\sim$3 Copoly(methylsilylene/*cis*- and *trans*-1,4-but-2-enylene/1,2-but-3-enylene). Physical Properties of Aliphatic Carbosilane Thermosets, Carbosilane/Carbon, and Carbosilane/Glass Composites

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Low molecular weight random copoly(methylsilylene/*cis*- and *trans*-1,4-but-2-enylene/1,2-but-3-enylene) (I) in which the ratio of methylsilylene units to *cis*- and *trans*-1,4-but-2-enylene units to 1,2-but-3-enylene units is approximately 2:1:1 has been prepared by the reaction of methyldichlorosilane, 1,3-butadiene, and magnesium in THF. Alternatively, random copolymers (II) in which the ratio of these units is approximately 2:$\sim$1:$\sim$3 can be prepared by a two-step reaction sequence. Copolymers I and II have been characterized by ^{1}H, ^{13}C, and ^{29}Si NMR as well as FT-IR spectroscopy. Their molecular weight distributions have been determined by gel permeation chromatography (GPC), their thermal stabilities in nitrogen evaluated by thermogravimetric analysis (TGA), and their glass transition temperatures (T_g) measured by differential scanning calorimetry (DSC). Platinum-catalyzed hydrosilylation cross-linking of I and II yields thermoset materials. The bending modulus (log E'), tan δ and T_g of these cross-linked materials have been measured by dynamic mechanical thermal analysis (DMTA). Carbon fabric has been treated with a mixture of either copolymer I or II and catalytic amounts of platinum. Multiple layers of coated carbon fabric have been consolidated (cured) to yield aliphatic carbosilane/carbon composite materials. Glass-reinforced composites have been prepared in a similar manner. The interlaminar shear strengths of these materials have been determined by short beam shear. Flexure strengths and moduli of elasticity of these composite samples have been measured. The ultimate compressive strengths and compression moduli as well as the tensile strengths and elastic moduli of these have been determined.

Introduction

Due to their commercial importance, there has been extensive work over the past 50 years on the chemistry of siloxane polymers.[1,2] On the other hand, there has been much less work done on carbosilane polymers. The proposal by Yajima in 1975 that copolymer(methylsilylene/methylene) is a key intermediate in the conversion of poly(dimethylsilane) fibers into silicon carbide fibers[3–5] has stimulated considerable interest in the chemistry of polycarbosilanes.[6,7]

The platinum-catalyzed addition of Si–H bonds of monomeric silanes across the C–C double bond of alkenes is a general method to prepare C–Si bonds.[8,9] Platinum catalyzed hydrosilylation polymerization of monomeric silanes which contain both Si–H groups and C–C double bonds to yield polycarbosilane has been reported.[10–12] Polysilanes which contain both reactive Si–vinyl and Si–H bonds have been prepared. On pyrolysis, these undergo thermal hydrosilylation cross-linking and high-yield conversion to β-silicon carbide.[17–19] Cross-linking has

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been shown to be an essential requirement for the high yield conversion of organometallic polymers to ceramic materials.[13–15]

We have previously utilized hydrosilylation cross-linking to convert linear aromatic carbosilane polymers or oligomers to thermoset materials.[20] In this paper, we will report the utilization of the platinum-catalyzed hydrosilylation cross-linking of unsaturated Si–H containing oligomers to form aliphatic thermoset materials. The hydrosilylation reaction constitutes a novel cure which permits the preparation of oxygen-free composite materials. Mechanical test data on such novel thermoset materials and laminated composite materials will be reported.

Experimental Section

^{1}H and ^{13}C NMR spectra were run on a Bruker AC-250 spectrometer operating in the FT mode. ^{29}Si NMR spectra were recorded on a Bruker 270-SY spectrometer. ^{13}C NMR spectra were run with broad-band proton decoupling. ^{29}Si NMR spectra were obtained by use of a heteronuclear gated decoupling pulse sequence (INVGATE) with a pulse delay of 15–20 s.[21] ^{13}C and ^{29}Si NMR spectra were obtained on 15% solutions in chloroform-*d*. ^{1}H NMR spectra were obtained on 5% solutions in chloroform-*d*. Chloroform was utilized as an internal standard for ^{1}H NMR spectra. Chloroform-*d* was used as an internal standard for ^{13}C NMR spectra. ^{29}Si NMR spectra were externally referenced to TMS. IR spectra of neat films on sodium chloride plates were recorded on an IBM FT-IR/30s, DTGS/CSI spectrometer. GC/MS was run on a Finnegan Mat Incos 50 GC/MS instrument at an ionizing voltage of 70 eV. A 0.25 mm × 30 m fused silica DB-5 capillary column was used in the gas chromatographic inlet of the mass spectrometer.

The molecular weight distribution of the unsaturated aliphatic carbosilane polymers was determined by GPC on a Waters system comprised of a U6K injector, a 510 HPLC solvent delivery system, a R401 differential refractometer and a Maxima 820 control system. Two Waters 7.8 mm × 30 cm Ultrastyragel linear columns, in series, packed with 1×10^4 Å and 1×10^3 Å particles of cross-linked styrene–divinylbenzene copolymer were utilized for the analysis. The eluting solvent was HPLC grade THF at a flow rate of 0.7 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: 47 500; 18 700; 5120 and 2200 whose M_w/M_n are less than 1.09.

TGA was carried out on a Perkin-Elmer TGS-2 instrument at a nitrogen flow rate of 40 cc/min. The temperature program for the analysis began at 50 °C for 2 min. The temperature was then increased at a rate of 5 °C/min to at least 650 °C. The T_g of the polymers were determined by DSC on a Perkin-Elmer DSC-7 instrument. The melting point of indium (156 °C) and of spectral grade *n*-hexane (−95 °C) were utilized to calibrate the DSC. The system was equilibrated at −100 °C for 5 min. The temperature was then increased at a rate of 20 °C/min to 150 °C.

The DMTA of cross-linked materials were performed on a Polymer Laboratories DMTA MkII. A standard single cantilever bending head (−150 to 300 °C) was used. The analysis was carried out at frequencies of 1 and 5 Hz at a strain level of 2. The initial temperature was generally 0 °C. After equilibration, the temperature was increased at 4 °C/min.

Short beam shear of composite laminates (ASTM D 2344-84) was carried out using a three-point fixture on an Instron model 1122 at a crosshead speed of 1 mm/min. The ratio of span length over sample thickness was 4:1.[22] The thickness and width of each sample was measured with a caliper to a precision of 0.001 in. Flexural tests (ASTM D 790-86) were carried out similarly except that the span to thickness ratio of the test samples was 16:1.[23]

Compressive strength was determined using a Northrop open-hole compression test fixture on an Instron as above according to SACMA (Suppliers of Advanced Composite Materials Association, Arlington, VA) method SRM-3-88 or Northrop Specification NAI-1504C, Northrop Corp. Hawthorne CA 5-1988. These are similar to ASTM D-3410-75.[24] Samples did not have a hole. A Micro-Measurement's strain gage type CEA-06-250UW-350 was bonded to the center of the test sample by use of M-Bond 200 Adhesive Kit (Measurements Group, Inc.) which contains methyl 2-cyanoacrylate and a catalyst system following the procedure in Instruction Bulletin B-127-12. The strain gage was connected to a Measurement Group/Vishay Digital Strain Indicator Model P-3500.

Tensile strength of composite laminates was determined (ASTM D-3039-76) on an Instron as above. Fiber glass epoxy tabs (3M type 1002) were bonded to the ends of the test samples using American Cyanamid FM-123 adhesive. A strain gage was attached to the center of the test sample as above.[25]

All reactions were carried out under an atmosphere of prepurified nitrogen in flame dried glassware. Ether and THF were distilled from a deep blue solution of sodium benzophenone ketyl immediately prior to use. Magnesium powder was obtained from Aldrich. 1,3-Butadiene was obtained from Matheson. Methyldichlorosilane and 1,3-divinyltetramethyldisiloxane Pt complex (2–3% Pt) (Pt complex) in xylene were obtained from Huls. Carbon fabric (Hercules AS4-6K 11×11 5H stain weave) was utilized. Glass fabric (Burlington Glass, file no. 1581, Finish I-501-112) was heated in a furnace at 350–400 °C for 24 h in air to burn off the finish. No degradation of the glass fabric was observed.

Synthesis of Random 2:1:1 Copoly(methylsilylene/*cis*- and *trans*-1,4-but-2-enylene/1,2-but-3-enylene) (I). In a 500-mL three-neck round-bottom flask equipped with a Teflon-covered magnetic stirring bar, an efficient reflux condenser and two rubber septa was placed magnesium powder (8 g, 0.33 mol), methyldichlorosilane (29 g, 0.25 mol), iodine (0.5 g), and THF (200 mL). The reflux condenser was connected to an external refrigeration unit. Isopropyl alcohol cooled to −20 °C was circulated through the condenser. 1,3-Butadiene (15.5 g, 0.29 mol) was condensed at −78 °C into a large test tube which was sealed with a rubber septum which contains granular anhydrous calcium chloride. After drying, the 1,3-butadiene was then transferred to the reaction flask via a cannula. **The reaction was quite exothermic.** The reaction flask was cooled in an ice/water bath. **In larger scale reactions, the exothermicity of the reaction can be controlled by slow addition of methyldichlorosilane via a pressure-equalizing addition funnel.** After the initial reaction had subsided, the reaction flask was allowed to warm to room temperature and was stirred overnight. The flask and its contents were then heated to 50 °C for 2 h. The mixture was cooled to room temperature and was filtered. This serves to remove unreacted magnesium and some salts. The filtrate was slowly added to 100 mL of an ice-cold saturated solution of aqueous ammonium chloride. The organic and aqueous layers were separated. The aqueous layer was extracted with ether (3 × 100 mL). The combined organic phase was washed with saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. The residue was fractionally distilled through a 15-cm vacuum jacketed Vigreux column. After removal of ether and THF, 1-methyl-1-silacyclopent-3-ene (bp 89 °C,[26] 3.7 g, 15% yield) was obtained. A second fraction composed of cyclic dimers (bp 86 °C/7 mmHg, 3.5 g, 14% yield) was collected. The residue was dissolved in a minimum amount of THF and was precipitated from methanol. In this way, 15 g, 60% of I was obtained. Evaporation of the solvents gave ~2 g (10%) of lower molecular weight I. The spectral properties of this lower molecular weight material were almost identical to that of I which had precipitated.

I has the following properties: $M_w/M_n = 3960/1920$, $T_g = -86$ °C. ^{1}H NMR δ: 0.07 (br s, 2.6H), 0.14 (br s, 0.4H), 0.75 (br s, 0.8H), 1.20 (d, 0.2H, $J = 17.5$ Hz), 1.33 (d, 0.2H, $J = 17.5$ Hz), 1.50 (br s, 3.2H), 1.79 (br s, 0.36H), 3.6–3.8 (br m, 0.9H), 4.88 (m,

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0.86H), 5.25 (s, 0.5H), 5.32 (s, 0.7H), 5.68 (m, 0.4H), 5.83 (br s, 0.2H). ^{13}C NMR δ: −8.9, −8.7, −8.4, −8.1, −6.9, −6.7, −6.4, −6.2, −5.9, −5.6, −3.9, −3.6, −1.7, −1.3, −0.8, −0.3, 9.8, 11.6, 11.9, 12.5, 12.6, 13.6, 13.8, 14.3, 15.7, 15.9, 16.2, 16.6, 17.2, 18.1, 18.4, 19.0, 22.6, 22.8, 25.1, 25.3, 26.7, 28.3, 29.6, 29.8, 111.8, 112.8, 121.3, 122.0, 122.8, 123.1, 123.8, 124.1, 124.6, 125.6, 126.4, 131.0, 139.1, 140.6. ^{29}Si NMR δ: −12.7, −12.3, −11.9, −11.2, −10.8, −10.2, −6.5, −6.1, −0.8, 16.8, 17.1. IR ν: 3070, 3010, 2959, 2884, 2115 (s), 1625, 1400, 1251, 1153, 1100, 995, 879 (br), 723 cm^{-1}.

The dimer fraction has the following spectral properties. ^{1}H NMR δ: 5.98 (m, 1H), 5.44 (m, 0.3H), 4.89 (d, 1H, J = 8 Hz), 4.87 (d, 1H, J = 14 Hz), 4.08 (s, 0.15H), 4.00–3.66 (br.m, 0.4H), 3.6 (s, 0.15H), 3.3 (s, 0.1H), 2.2–1.9 (m, 0.2H), 1.74 (br.s, 0.6H), 1.59 (m, 0.6H), 1.05 (br.s, 0.8H), 0.9–0.7 (br m, 0.8H), 0.12 (s, 2H), 0.04 (s, 1H). ^{13}C NMR δ: −8.8, −7.3, −6.8, −5.3, −5.0, −4.7, 11.2, 11.6, 11.9, 12.3, 13.0, 13.56, 13.6, 14.2, 14.3, 14.4, 14.8, 14.9, 15.0, 15.1, 15.2, 24.3, 25.8, 26.3, 26.4, 26.8, 27.3, 27.6, 29.1, 29.2, 110.0, 110.1, 110.2, 110.24, 110.3, 110.4, 110.5, 110.7, 111.1, 111.5, 111.6, 122.7, 122.9, 123.0, 130.9, 140.2, 141.6, 141.7, 142.0, 142.2, 142.3, 142.4, 142.5, 143.3. ^{29}Si NMR δ: −16.3, −10.6, −5.8, −3.3. IR ν: 3065, 3040, 3000, 2980, 2970, 2960, 2880, 2860, 2100 (s), 1640, 1410, 1400, 1250, 1165, 1060 (br), 985, 920, 860 (br), 810, 720 cm^{-1}. GC/MS m/e (rel intensity): 196 (1), 195 (4), 181 (5), 168 (18), 155 (9), 153 (8), 141 (10), 140 (10), 127 (22), 113 (7), 98 (27), 97 (100), 96 (30), 95 (23), 83 (28), 71 (20), 59 (10), 55 (15).

Synthesis of Random 2:∼1:∼3 Copoly(methylsilylene/*cis*- and *trans*-1,4-but-2-enylene/1,2-but-3-enylene) (II). A 500-mL three-neck round bottom flask was equipped with a Teflon-covered magnetic stirring bar, an efficient reflux condenser which was connected to an external refrigeration unit as above. Two of the necks of the flask were sealed with rubber septa. A thermometer extended into the flask through a small hole in one of the septa. Magnesium powder (2.9 g, 0.12 mol), iodine (0.3 g), and THF (150 mL) were added to the flask. 1,3-Butadiene (0.12–0.25 mol) was condensed at −78 °C and dried as above. The 1,3-butadiene was transferred to the reaction flask via a cannula. The resulting mixture was stirred for 15–48 h at 50–70 °C. Various ratios of starting materials were used (see Table II). The reaction mixture was cooled to 0 °C in an ice/water bath. Methyldichlorosilane (0.1 mol) was slowly added to the flask so that the reaction temperature was maintained below 20 °C. **The reaction was quite exothermic.** After completion of the addition, the reaction was stirred at room temperature for 12 h and then was heated at 50 °C for 2 h. The reaction mixture was filtered through a Buchner funnel as above. The filtrate was slowly added to an ice cold solution of saturated aqueous ammonium chloride (80 mL). The layers were separated and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic phase was washed with saturated aqueous sodium chloride, dried over anhydrous magnesium sulfate. After filtration, the ether solvents and 1-methyl-1-silapent-3-ene were removed by fractional distillation. The residue, was dissolved in a minimum amount of THF and II was precipitated from methanol. A mixture of dimers and low molecular weight oligomers remains in the methanol and THF solvent. M_w/M_n = 1790/1270 T_g = −81 °C. ^{1}H NMR δ: 5.9–5.6 (br m, 1.7 H), 5.4–5.2 (br s, 1.9 H), 5.0–4.75 (br m, 3.4 H), 3.7–3.5 (br s, 0.65 H), 2.2–1.4 (br m, 10 H), 0.9(d, 1 H, J = 5 Hz), 0.1 (s, 0.3H), 0.04 (s, 3.1 H). ^{13}C NMR δ: −8.1, −7.5, −7.2, −6.2, −6.0, −4.7, 13.4, 13.7, 14.5, 15.8, 16.2, 17.7, 17.9, 18.0, 18.2, 18.6, 19.5, 26.6, 27.1, 27.2, 27.3, 27.4, 27.5, 27.7, 29.5, 29.6, 29.8, 30.0, 30.7, 30.8, 31.0, 31.2, 31.3, 31.7, 31.9, 32.0, 32.8, 33.0, 33.1, 33.2, 33.8, 35.3, 109.4, 109.5, 109.6, 109.7, 109.8, 112.4, 112.8, 112.9, 113.8, 113.9, 124.2, 124.3, 124.8, 125.0, 125.4, 125.9, 127.5, 127.6, 127.9, 129.3, 130.8, 131.1, 139.3, 139.5, 139.7, 139.8, 139.9, 140.0, 140.3, 140.4. ^{29}Si NMR δ: −12.3, −8.7, −8.6, −7.8, −5.5, −5.1, 14.9, 15.6, 18.3, 19.4. IR ν: 3078, 3007, 2923, 2856, 2112, 1639, 1626, 1450, 1413, 1251, 1154, 1100, 1061, 996, 965, 893, 720 cm^{-1}.

Hydrosilylation Cross-Linking of Unsaturated Aliphatic Carbosilane Polymers. A steel mold (3.5 in. × 1.5 in.) with removable sides was coated with liquid release agent (Airtech, Release-all 100H) and was heated to 130 °C for 1 h. This process was repeated. A mixture of polymer (4.0 g), 100 μL of Pt catalyst and 10 mL of ether was placed in a 50-mL round-bottom flask. Most of the solvent was removed by evaporation under reduced pressure. The concentrated polymer solution was poured into the mold which was put in a vacuum drying oven. The oven was heated to 50 °C at a pressure of 10^{-1} mmHg to remove residual solvent. After 1 h, the temperature of the oven was raised to 150 °C for 3 h. At this time, the polymer sample had become quite viscous. The oven was opened and the mold was sealed with a closely fitting piece of steel which has been previously treated with release agents. The steel seal applies a pressure of 0.6 psi to the polymer sample. The sealed mold is placed between the platens of a heated hydraulic press at 150 °C for 1 h. A pressure of 300 psi was then applied to the sealed mold and the temperature was slowly increased from 150 to 200 °C over 16 h. The press was opened and the mold and its contents were slowly cooled from 200 °C to room temperature over 8 h. This constitutes the standard initial cure. Rapid cooling may result in cracking of the samples. The sides of the mold were removed and the cross-linked sample was removed from the mold with an Exacto knife or single-edge razor blade. In some cases the cross-linked sample was placed in a vacuum oven and subjected to further heat treatment at 200–240 °C for 24–90 h. Slow cooling was again essential. The sample was cut to size. Samples for DMTA were generally about 25 × 10 × 2 mm. For DMTA data of I and II after treatment by various cure cycles, see Figures 1 and 2.

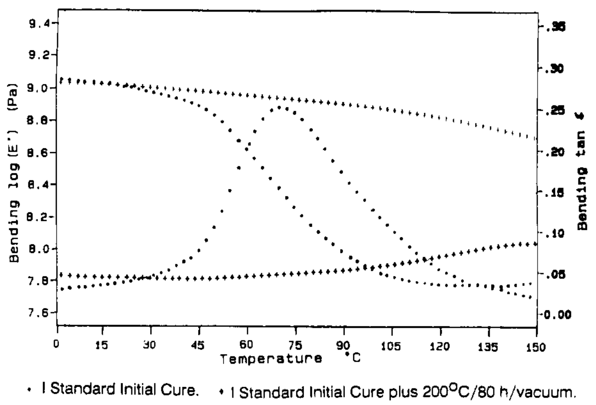


Figure 1. DMTA of platinum-cured I. (●) I standard initial cure. (+) I standard initial cure plus 200 °C/80 h/vacuum.

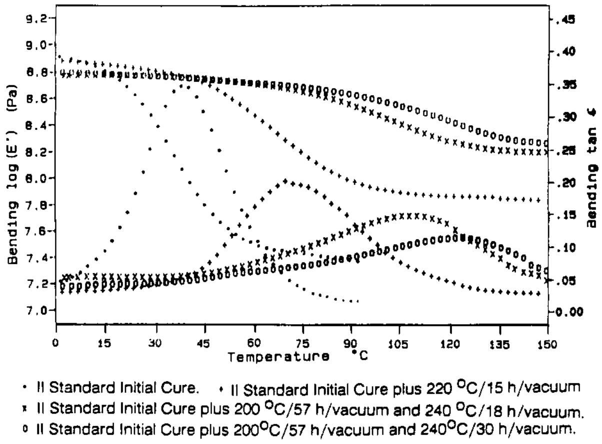


Figure 2. DMTA of platinum-cured II. (●) II standard initial cure. (+) II standard initial cure plus 220 °C/15 h/vacuum. (×) II standard initial cure plus 200 °C/57 h/vacuum and 240 °C/18 h/vacuum. (○) II standard initial cure plus 200 °C/57 h/vacuum and 240 °C/30 h/vacuum.

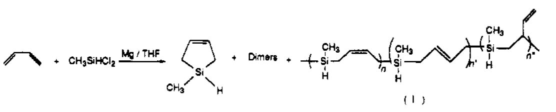
Preparation of Composite Samples. A steel mold was coated with liquid release agent and was heated as above. This process was repeated. Release films (Airtech Release Ease 234 TFP and Thermalimide RCBS) were placed in the mold. Carbon fabric was cut to the dimensions of the steel mold (3.5 in. × 1.5 in.). Eight layers of carbon fabric (∼9.6 g) were placed in the mold and were treated with 150 μL of Pt complex and I (9–10 g) dissolved in 20 mL of ether. Ether was removed by evaporation at 50 °C in a vacuum drying oven for 1 h. A second set of release films was placed above the stack of carbon fabric. The mold is then closed with a steel seal (3.5 in. × 1.5 in.) which weighs 3 pounds and has been previously treated with release agents as above. The sealed mold and its contents are then heated to 125 °C under 0.6 psi of pressure for about 1 h. Some of the polymer matrix materials (~2 g) flows out of small cracks where the removable sides of the mold are sealed. During the 1 h, the polymer matrix begins to cross-link. The flow of polymer materials from the mold then decreases.

The mold is then placed between the heated (125 °C) plattens of a hydraulic press. A pressure of 300 psi is applied to the mold. The temperature is increased to 210 °C over 1 h and is then held constant for 15 h. The mold was then cooled to room temperature over 12 h while pressure was maintained. The composite sample was removed from the mold and weighed. This permits calculation of the percent matrix in the composite—usually 25–45%. Samples were cut using a water cooled diamond saw: 3 mm × 12 mm × 20 mm for short beam shear, 3 mm × 25 mm × 80 mm for flexure, 3 mm × 12 mm × 76 mm for compression and 2 mm × 12 mm × 76 mm for tensile measurements.

Fiber glass composite samples were prepared in a similar manner.

Results and Discussion

The reaction of disubstituted dichlorosilanes with 1,3-butadiene and magnesium in ether solvents generally leads to high yields of 1,1-disubstituted-1-silacyclopent-3-enes. For example, diphenyldichlorosilane gives 1,1-diphenyl-1-silacyclopent-3-ene in almost quantitative yield under these conditions.[27] On the other hand, reaction of Si–H substituted dichlorosilane such as methyldichlorosilane and phenyldichlorosilane with 1,3-butadiene and magnesium give much lower yields of 1-silacyclopent-3-enes. For example, the reaction of phenyldichlorosilane with 1,3-butadiene and magnesium gives a 20% yield of 1-phenyl-1-silacyclopent-3-ene.[28] We have found that the yield of 1-substituted-1-silacyclopent-3-enes significantly depends on whether ether or THF are used as the solvent. Thus a 35% yield of 1-methyl-1-silacyclopent-3-ene is obtained in ether, whereas the yield in THF is only 10–15%. The residue, when THF solvent is used, after removal of 1-methyl-1-silacyclopent-3-ene is made up a mixture of cyclic dimers (10–15%) and predominantly linear oligomer (I), 60–70%, eq 1).



(1)

By GC/MS there are at least ten dimers detectable. All of these have similar mass spectra. In addition to the parent ion at $m/e = 196$, siliconium ions formed by loss of a hydrogen or methyl group from the silyl center are observed at $m/e = 195$ and $m/e = 181$, respectively. The base peak at $m/e = 97$, is equal to half the molecular weight − 2. This ion may in fact be a doubly positively charged *bis*siliconium ion formed by loss of the two hydrogen atoms from the silyl centers (Figure 3).

^{1}H, ^{13}C, and ^{29}Si NMR spectra have been taken of the mixture of dimers. Signals in the ^{1}H NMR at 5.9 and 4.9 ppm in a 1:2 integration ration are characteristic of terminal vinyl groups. Eleven peaks between 110.0 and 111.6 ppm and nine peaks between 140.2 and 143.3 ppm in the ^{13}C NMR are observed. These are characteristic of terminal vinyl units. On this basis, we believe that the dimers are predominantly 1,4-dimethyl-2,6-divinyl-1,4-disilacyclohexanes and 1,4-dimethyl-2,5-divinyl-1,4-disilacyclohexane isomers. The resonance at 5.4 ppm in the ^{1}H NMR is characteristic of the vinyl hydrogen of a *cis*- or *trans*-1,4-but-2-enylene unit. The ^{13}C NMR resonances at 122.7, 122.9, and 123.0 ppm are diagnostic for such units. If the minor isomers contain such *cis*- or *trans*-1,4-but-2-enylene units, they may be 2-vinyl-1,4-disilacyclooct-6-enes or 1,5-disilacyclodeca-3,8-dienes (Figure 4). 1,5-Disilacyclo-3,8-dienes have been previously isolated from the reaction of dimethyldichlorosilane, isoprene and lithium metal in THF.[29]

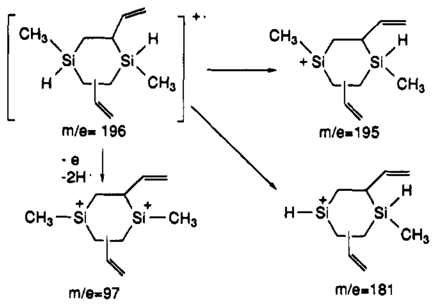


Figure 3. Predominant ions in the mass spectra of dimers.

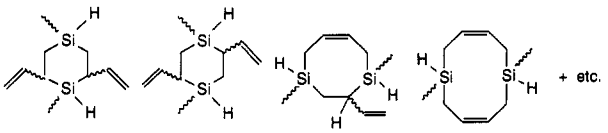


Figure 4. Possible structures of cyclic dimers.

The ^{1}H, ^{13}C, and ^{29}Si NMR and FT-IR spectra of **I** are consistent with a polymer ($M_W/M_n = 3960/1920$) comprised of methylsilylene, *cis*- and *trans*-1,4-but-2-enylene and 1,2-but-3-enylene units and 1-methyl-1-silacyclopent-3-ene end groups. The formation of this mixture of products can be rationalized in terms of a mechanism in which butadienyl anion radicals are primary intermediates. These are formed by electron transfer from magnesium to 1,3-butadiene. The coupling reaction of these with methyldichlorosilane may be faster in THF than in ether. THF is more basic than ether and better able to coordinate with magnesium cations. A second electron transfer from magnesium to the 4-methylchlorosilylbut-2-enyl allylic radical will lead to 4-methylchlorosilylbut-2-enyl anion. This allylic anion can react by nucleophilic displacement with Si–Cl bonds at either end of the allylic anion system. If the stereochemistry of this allylic anion is *cis*, it may react intramolecularly by cyclization to yield 1-methyl-1-silacyclopent-3-ene. Alternatively, intermolecular reaction with another molecule of methyldichlorosilane will yield 1,4-*bis*(methylchlorosilyl)-*cis*-but-2-ene (A). If the stereochemistry of the 4-methylchlorosilylbut-2-enyl anion has a *trans* configuration it will react with another molecule of methyldichlorosilane to yield 1,4-*bis*(methylchlorosilyl)-*trans*-but-2-ene (B). Finally the 4-methylchlorosilylbut-2-enyl anion can react at the 2 position of the allylic anion to yield 1,2-*bis*(methylchlorosilyl)but-3-ene (C). These intermediates can react further with butadienyl anion radicals to lead to the mixture of dimers and oligomers which are isolated (Figure 5). The ratio of methyldichlorosilane to 1,3-butadiene and magnesium has very little effect on the composition of I formed (Table I). The percent Si–H, 1,2-but-3-enylene, and 1,4-but-2-enylene

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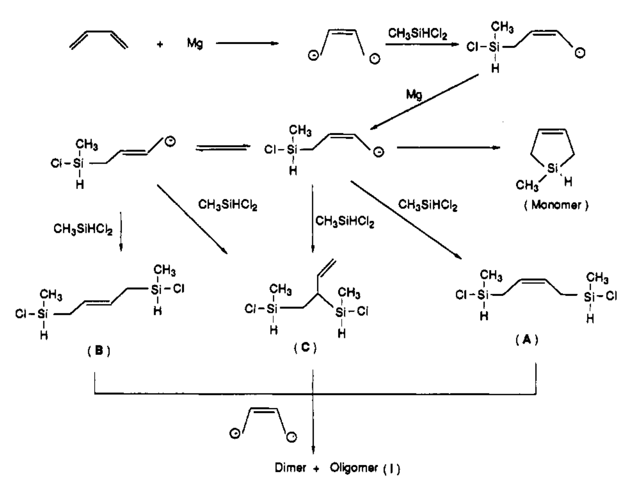


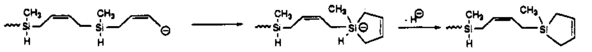
Figure 5. Mechanism of formation of 1-methyl-1-silacyclopent-3-ene, dimers and I.

Table I. Effect of Molar Ratio of Starting Materials on the Composition and Molecular Weight of I

molar ratio							
CH_3SiHCl_2	butadiene	Mg	yield (%)	M_w/M_n	SiH (%)	1,2-but-3-enylene (%)	1,4-but-2-enylene (%)
1	1.1	1.3	60	3970/1920	90	42	58
1	1.6	1.5	42	3120/1775	70	46	54
1	3	1.2	55	2550/1440	75	51	49
1	1	1.5	62	3300/1990	85	46	54
1	1.3	1.2	55	2520/1220	90	43	57

units are determined by integration of the appropriate ^1H NMR signals relative to those of the methyl groups bonded to silicon.

Reaction of a butadienyl anion radical with intermediate A will yield 5-methyl-9-methylchlorosilyl-5-sila-*cis*-non-7-en-2-enyl radical. A second electron transfer from magnesium will lead to this allylic radical will lead to corresponding allylic anion. This can back bite by attacking silicon-5 to form a hypervalent five-membered heterocyclic siliconate anion which can lose hydride to form a terminal methyl-1-silacyclopent-3-ene end group as outlined in eq 2.


(2)

Evidence for the presence of 1-methyl-1-silacyclopent-3-ene end groups has been previously described in the discussion of the spectra of poly(1-methyl-1-sila-*cis*-pent-3-ene), prepared by the anionic ring opening polymerization of 1-methyl-1-silacyclopent-3-ene.[26] ^1H NMR signals at 5.83 (s), 1.33 (d, $J = 17.5$ Hz), 1.20 (d, $J = 17.5$ Hz) and 0.14 (s) ppm are interpreted as arising from 1-methyl-1-silacyclopent-3-ene end groups. Signals at 131.0, 15.9, 15.7, −3.6, and −3.9 ppm in the ^{13}C NMR as well as resonances at 17.1 and 16.8 ppm in the ^{29}Si NMR are similarly assigned. 1-Methyl-1-silacyclopent-3-ene rings bonded to *cis*-1,4-but-2-enylene groups have been previously found to give ^{13}C NMR signals at 130.9, 16.46, 15.45, and −3.76 ppm and a ^{29}Si signal at 17.1 ppm.[26]

The methylsilylene units give rise to a broad singlet centered at 0.07 ppm due to the methyl group and a broad signal centered at 3.78 ppm due to the Si–H in the ^1H NMR. The methyl group gives rise to sixteen signals in the ^{13}C NMR between −8.9 and −0.3 ppm. The methyl carbon of stereoregular poly(1-methyl-1-sila-*cis*-pent-3-ene) is found at −6.36 ppm.[26] The methyl carbon bonded to silicon in these polymer systems must be highly sensitive to microenvironment. The signals at −12.7, −12.3, and −11.9 ppm may be assigned to methylsilylenes which have two *cis*-1,4-but-2-enylene bond to silicon, to methylsilylenes which have one *cis*-1,4-but-2-enylene and one *trans*-1,4-but-2-enylene units bonded to silicon and finally to methylsilylenes which have two *trans*-1,4-but-2-enylene units bonded to silicon. For comparison, the ^{29}Si in the stereoregular poly(1-methyl-1-sila-*cis*-pent-3-ene) is found at −12.7 ppm.[26] The resonances at −11.2, −10.8, −10.7, and −10.4 ppm may be assigned to methylsilylene units which have *cis*- or *trans*-1,4-but-2-enylene on one side and 1,2-but-3-enylene units on the other. The resonances at −6.5, −6.1, and 5.95 ppm may be assigned to methylsilylene units which have two 1,2-but-3-enylene units bonded to silicon (Figure 6).

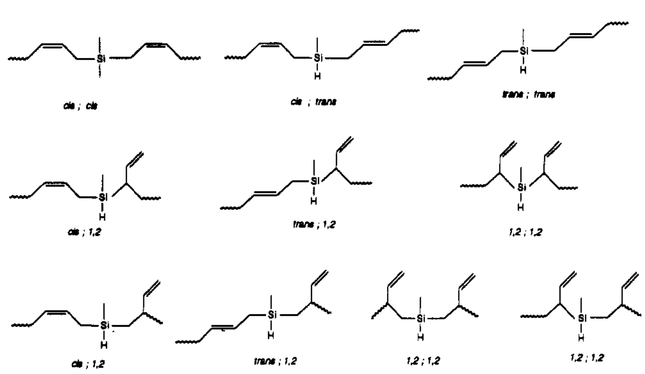
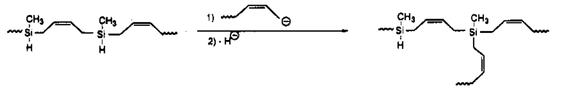


Figure 6. Microstructures of methylsilylene units.

Finally, the small signal at −0.8 ppm is probably due to silicon in which hydride has been displaced by an allylic anion as outlined below. It is well-known that hydride can serve as a leaving group from silyl centers.[30,31] Apparently, oligomer I has at least a few branch points. The presence of branch points as well as 1-methyl-1-silacyclopent-3-ene end groups leads to less than 100% Si–H groups in I (eq 3).


(3)

The *cis*-1,4-but-2-enylene units give rise to signals at 5.33 and 1.5 ppm in the ^1H NMR. Several intense signals between 13.6 and 14.3 ppm in the ^{13}C NMR are assigned to the *cis* allylic carbons. The *trans*-1,4-but-2-enylene units give rise to signals at 5.26 and 1.5 ppm in the ^1H NMR. Signals at 18.1, 18.4, and 19.0 ppm in the ^{13}C NMR are assigned to the *trans* allylic carbons. The similar chemical shift differences for allylic carbons have been observed in *cis* and *trans* allylic silanes.[32,33] Nine signals between 121.3 and 126.4 ppm in the ^{13}C NMR are assigned to the vinyl carbons of *cis*- and *trans*-1,4-but-2-enylene units. These are apparently sensitive to microstructure.

The 1,2-but-3-enylene units give rise to signals at 0.75, 1.79, 4.9, and a broad resonance centered at 5.7 ppm in the ^1H NMR. In the ^{13}C NMR spectrum: C_1 gives rise to resonances at −1.7 and −0.3 ppm, C_2 to signals at 22.6 and

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Table II. Effect of Molar Ratio of Starting Materials and Reaction Conditions of Magnesium with Butadiene on the Composition and Molecular Weight of II

molar ratio butadiene	 Mg	reaction conditions (step 1)	CH_3SiHCl_2 (step 2)	yield (%)	M_w/M_n	SiH (%)	1,2-but-3-enylene (%)	1,4-but-2-enylene (%)
1.25	2.7	70 °C/18 h	1	80	2670/1850	88	104	42
1.4	2	65 °C/42 h	1	52	1730/1220	95	135	65
1.5	1	50 °C/30 h	1	58	4415/2450	84	125	45
1.5	1.2	60 °C/24 h	1	65	4033/2340	92	125	38
2.5	1.2	70 °C/48 h	1	70	1790/1270	85	146	87
1.5	1.5	40 °C/4 h	1	68	2100/1260	93	52	48

22.8 ppm, and C_3 and C_4 to resonances at 111.8, 112.8, 139.1, and 140.6 ppm.

Random 2:~1:~3 copoly(methylsilylene/*cis*- and *trans*-1,4-but-2-enylene/1,2-but-3-enylene) (**II**) has been prepared by reaction of a 1:2 magnesium:1,3-butadiene complex. 1:1, 1:2, and even 1:3 magnesium:1,3-butadiene complexes have been previously reported.[34-39] Reaction conditions, i.e., time, temperature, and stoichiometry apparently affects the ratio of these magnesium:1,3-butadiene complexes which are formed. This in turn affect the ratio of *cis*- and *trans*-1,4-but-2-enylene units to 1,2-but-3-enylene units which are observed (Table II). When the reaction is carried out for *short times* at 40 °C rather than a higher temperature, **I** is formed rather than **II**. We believe that this report is the first example of the utilization of such magnesium:1,3-butadiene complexes as a reagent to form oligomers or polymers.

The microstructure of **II** can be partially elucidated by ^1H, ^{13}C, and ^{29}Si NMR spectroscopy. Broad multiplets centered at 5.7 and 4.85 ppm in a 1:2 integration ratio and ^{13}C NMR signals between 109 and 114 ppm as well as between 139 and 140.5 ppm are characteristic of the of the terminal vinyl groups of the 1,2-but-3-enylene units. The major peak in the ^{29}Si NMR occurs as a multiplet centered at −8.7 ppm. A broad multiplet centered at 5.35 ppm in the ^1H NMR and ^{13}C NMR signals between 124 and 128 ppm are characteristic of *cis*- and *trans*-1,4-but-2-enylene units. Resonances due to 1-methyl-1-silacyclopent-3-ene end groups are observed in the ^{13}C NMR at 130.8 and 131.1 ppm.

The structure of **II** is much more complex than **I**. **II** is prepared by a two step process. In the first, a mixture of 1:1, 2:1, and 3:1 butadiene:magnesium complexes are prepared in which the 2:1 is major. These are *bis*allylic Grignard reagents. The structure of the 1:1 complex is probably a five-membered heterocycle, 1-magnesiocyclopent-3-ene. On the other hand, there are, in addition to linear structures, at least six cyclic structures for the 2:1 complex (D–I). The preponderance of 1,2-but-3-enylene units in II may reflect the selective formation of 2:1 complexes G–I (Figure 7). There are even more structures for the 3:1 complexes. All of these can and do react with methyldichlorosilane.

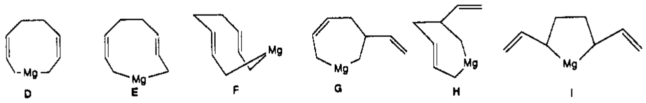

Figure 7. Possible cyclic structures of 2:1 complexes of 1,3-butadiene and magnesium.

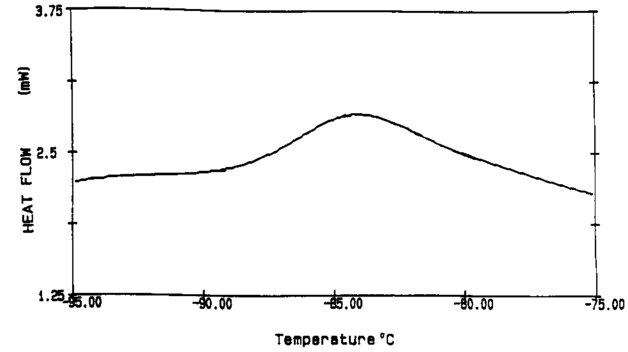

Figure 8. DSC of **I**.

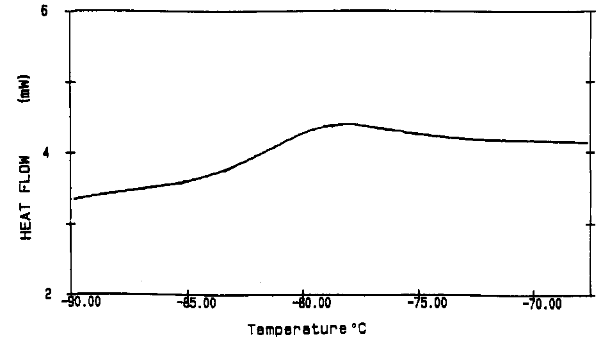

Figure 9. DSC of **II**.

Key structural features of both **I** and **II** is that they both contain Si–H and terminal vinyl groups. Hydrosilylation cross-linking is much more facile with terminal vinyl groups than with internal carbon–carbon double bonds. For this reason, initial hydrosilylation crosslinking cure of both **I** and **II** are relatively easy to achieve.

The T_g's of both **I** and **II** are low. The T_g for **I** is −86 °C while that for **II** is found to be −81 °C (see Figures 8 and 9).

The thermal stability of **I** has been determined by TGA. **I** is thermally stable to 140 °C. Between 140 and 220 °C a 4% weight loss occurs. Above this temperature a slow weight loss of an additional 4% occurs until 420 °C. Above 420 °C rapid weight loss occurs. By 540 °C only 24% of the initial sample weight remains. The thermal stability of platinum catalyzed cross-linked samples of **I** have also been determined by TGA. They are essentially the same as **I** except that the initial weight loss is eliminated. Virtually no weight loss of Pt cross-linked samples of **I** occurs before 380 °C. We believe that thermal stability of 92% of the initial sample weight of **I** results from cross-linking via thermal hydrosilylation reactions. Apparently the thermal stability of the crosslinked material is similar whether this is produced by thermal or platinum-catalyzed hydrosilylation reactions (Figure 10).

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Table III. Physical Properties of Carbosilane/Carbon and Carbosilane/Glass Composites

		short-beam shear		flexure			tensile			compression		
polymers	fabric	S_H (kpsi)	matrix (%)	S_F (kpsi)	modulus of elasticity bending (Mpsi)	matrix (%)	ultimate tensile strength (kpsi)	modulus of elasticity (kpsi)	matrix (%)	ultimate compression strength (kpsi)	compression modulus (kpsi)	matrix (%)
I	carbon	2.5	28	49	4.9	28	27	904	25	30	1070	28
II	carbon	2.8	43	38	5.4	43	17	1117	25	27	1540	38
I	glass	2.9	25	29	1.8	25	12	274	25	19	250	25
II	glass	3.3	28	25	1.8	28	14	394	25	27	480	28

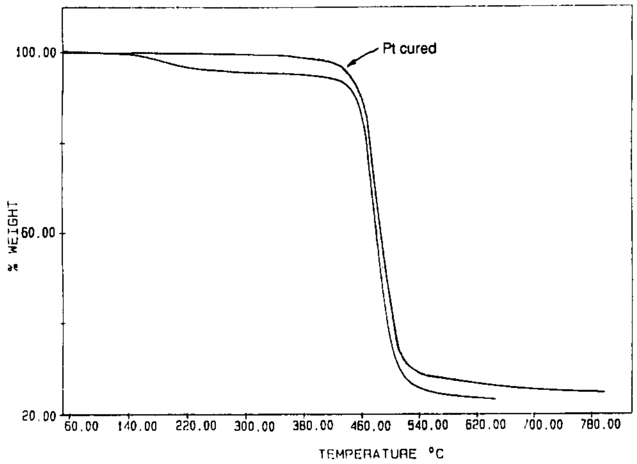

Figure 10. TGA of I.

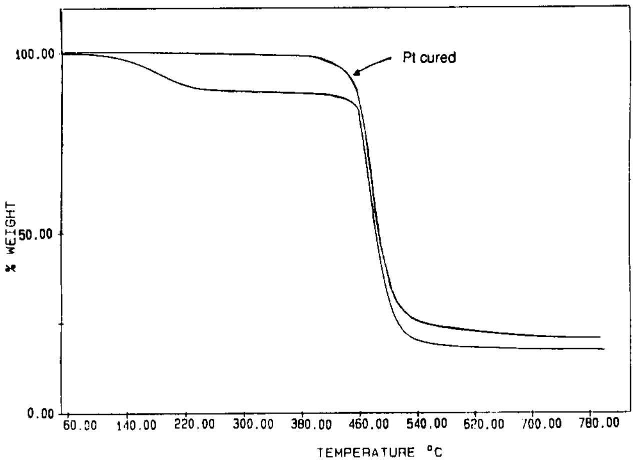

Figure 11. TGA of II.

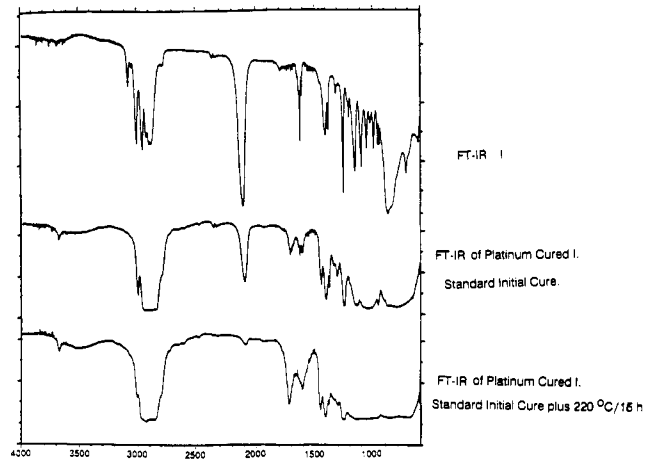

Figure 12. Progress of platinum-catalyzed hydrosilylation cure of **I** by FT-IR. Disappearance of the Si–H stretch at ~2100 cm^{-1}.

The thermal stability of **II** has likewise been determined by TGA. **II** is thermally stable to 100 °C. Between 100 and 220 °C a loss of about 8% of the initial sample weight is lost. Between 220 and 420 °C virtually no weight change is detected. Above 420 °C rapid weight loss occurs. By 540 °C only a 20% residue is left. No furhter weight loss occur on heating the sample to 800 °C. The thermal stability of platinum catalyzed crosslinked samples of **II** are similar, expect that no weight loss occurs below 420 °C. It is surprising that more than 90% of the initial weight of low molecular weight **II** is thermally stable to 420 °C. We believe that this stability results from cross-linking by thermal hydrosilylation reactions. The cross-linked material produced by thermal and platinum-catalyzed hydrosilylation reactions has similar thermal stability (Figure 11).

The progress of the platinum-catalyzed hydrosilylation reaction can be followed by FT-IR (Figure 12).

The bending modulus log E', tan δ and T_g of the Pt cross-linked samples of **I** and **II** were determined by DMTA at both 1 and 5 Hz. The value of T_g observed depends on the frequency utilized. The T_g's, observed are generally about 5 °C higher when determined at 5 Hz than T_g's determined at 1 Hz. Whereas the value of tan δ is virtually the same. At temperatures which are at least 20 °C below T_g, the bending modulus log E' is constant between 8.8 and 9.2 Pa. The value of log E' decreases rapidly above this temperature and reaches a new plateau region at about twenty degrees above T_g. Thus these polymeric cross-linked materials show regions of both glassy and rubbery properties. In general, increasing the length of time and temperature of the cure cycle leads to an increase in cross-linking. This is reflected in a decrease in tan δ and an increase in T_g. The T_g of **I** is higher than that of **II** and tan δ is lower for **I** than **II** after comparable cure cycles. This probably reflects the fact that the crosslink density of **I** after curing is higher than **II**. This is reasonable since **I** has approximately one Si–H for every unit of unsaturation, whereas **II** only has approximately one Si–H for every two units of unsaturation. On the other hand, increased cure time and temperature have little effect on the bending modulus log E' measured for cross-linked polymer in the glassy region. Increased cure time and temperature result in an increase of the value of log E' in the rubbery region. In fact, if the cross-linking is increased sufficiently by curing for very long times at high temperature only a glassy region is observed (Figure 1 and 2).

Composite materials are made up of matrix and reinforcing fibers.[40–42] Matrix materials can be thermoplastics

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which have high T_g's or polymers which can be cross-linked to yield thermoset materials. Fiber glass or carbon fiber are often used. Coupling agents are frequently utilized to minimize the incompatibility between matrix and fibers which leads to failure at the interface.[43] We have prepared novel composite materials which utilize platinum catalyzed hydrosilylation cross-linked carbosilane oligomers **I** or **II** as matrix and carbon or glass fabric for reinforcement. No coupling agents were used.

The interlaminar shear strength (S_H) of carbon fabric composites of **I** and **II** as well as of glass fabric composites of **I** and **II** have been determined by short beam shear. The flexural strength and modulus of elasticity in bending of similar samples has been determined as well as the ultimate compressive strength and their compression modulus. Finally, the ultimate tensile strength and their elastic modulus have been measured. It is surprising that the values of these physical properties are similar for carbon **I** and carbon **II** composites since the ultimate cross-link density for **I** should be twice as great as for **II** as was observed by DMTA (Figures 1 and 2). Likewise, the values of these physical properties for glass **I** and glass **II** composites are quite similar. In general the values of the physical properties for the carbon fabric composites are greater than those of the glass fabric composites. This may reflect the fact that the physical properties of carbon fabric are stronger than those of glass fabric (Table III).

The mechanical properties of these composites are less than those of epoxy/carbon or epoxy/glass composites by a factor of approximately 10. Considering the enormous quantity of work which has been done on epoxy composites for the past 40 years, we believe that these initial results warrant further work on carbosilane polymers as matrix materials.

Acknowledgment. This work was support by DARPA/Office of Naval Research.

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