Macromolecules **1993,** *26,* 5671–5675

Catalytic Synthesis of Silylene–Vinylene Preceramic Polymers from Ethynylsilanes

Y. Pang, S. Ijadi-Maghsoodi, and T. J. Barton*

Ames Laboratory (U.S. Department of Energy) and Department of Chemistry, Iowa State University, Ames, Iowa 50011

Received February 26, 1993; Revised Manuscript Received June 24, 1993⊗

ABSTRACT: Catalytic hydrosilylation of diorganoethynylsilanes, $R_2HSiC{\equiv}CH$, with H_2PtCl_6 cleanly affords soluble poly(silylenevinylenes), $-(R_2SiCH{=}CH)_n-$, which were characterized by ^1H NMR, ^{13}C NMR, ^{29}Si NMR, FT-IR, GPC, and TGA. Bulk pyrolysis of these polymers under an inert atmosphere at temperatures above 1100 °C resulted in the formation of silicon carbide powders as characterized by X-ray diffraction spectra. Melt-spun fibers from these polymers were surface cross-linked and then thermally converted to SiC fibers with a dense surface microstructure.

Introduction

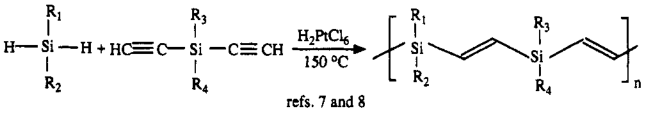
In recent years a number of organosilicon polymers have been developed whose thermal decompositions produce ceramic materials containing varying amounts of silicon carbide (SiC).[1] "Polycarbosilane", a polymer of indefinite structure produced by thermally isomerizing the product of sodium-induced condensation of Me_2SiCl_2, is pyrolyzed to produce Nicalon, the only commercial small-diameter, continuous SiC fiber.[2] A variety of linear polysilanes[3] and polycarbosilanes[4,5] have been reported but, as they tend to depolymerize on heating and afford little or no ceramic yield, they are not useful SiC precursors. In order to increase ceramic yield, functionalities which afford thermal cross-linking are needed in the polymer. Polysilaethylene,[6] prepared by the ring-opening polymerization of 1,3-disilacyclobutane, pyrolyzes with 87% ceramic yield as a result of the presence of Si–H functionality which cross-links the polymer at lower temperatures than those required for depolymerization. The presence of unsaturation in the polymer main chain should also allow for relatively low-temperature cross-linking, and indeed linear silylene–acetylene polymers[7] are thermally converted with high char yields[7a] to SiC (and varying amounts of carbon depending upon the substituents on silicon) with no volatilization of the backbone silicon or acetylenic carbons. Presumably this result is due both to thermal cross-linking and to the considerably greater bond strength of the silicon–acetylene bond relative to either a silicon–silicon or silicon–alkyl bond. To establish whether this dramatic effect on polymer degradation brought about by the inclusion of sp-hybridized carbons in the chain extends to sp^2 carbons, we have sought and report here an efficient route to silylene–vinylene, $-(R_2SiCH{=}CH)_n-$, polymers.

Results and Discussion

In 1962, and again in 1965, Luneva et al.[8,9] reported that condensation of methylphenylsilane and aryldiethynylsilanes in the presence of catalytic amounts of chloroplatanic acid (CPA) produced low molecular weight polymers 1 and 2 (Scheme I) with alternating Si and C=C double bonds in the main chain, which were slightly soluble in benzene.

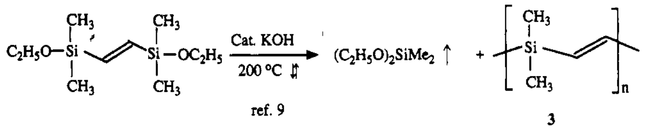
Andrianov in 1966 reported a synthetic route to silvinylene polymers involving catalytic redistribution.[10] The disproportionation of bis(dimethylethoxysilyl)ethylene in the presence of a catalytic amount of potassium hydroxide at 200 °C produced diethoxydimethylsilane and soluble brown polymer claimed to be dimethylsilylene–vinylene polymer **3**, although no molecular weight or spectroscopic characterization was reported for this polymer (Scheme II).

Scheme I



Polymer No.	R_1	R_2	R_3	R_4	M_w
1	CH_3	Ph	CH_3	Ph	?
2	CH_3	Ph	Ph	Ph	6000

Scheme II



Both literature routes suffer from inadequately characterized products and harsh reaction conditions which would be expected to produce side reactions. We have spent considerable effort attempting to improve the hydrosilylation route of Luneva only to find that at moderate temperatures the reported monomers only cyclize and oligomerize, resulting in loss of the necessary stoichiometric equality of the hydride and acetylene functionalities. At higher temperatures these cyclics and oligomers undergo secondary reactions to produce irregular polymeric materials. As incorporation of both the hydride and ethynyl on a single silicon monomer guarantees perfect 1:1 stoichiometry, as well as simplifying the reaction by reducing the number of reagents, a study of CPA-catalyzed hydrosilylation of dialkylethynylsilanes was undertaken as a potential route to silylene–vinylene polymers.

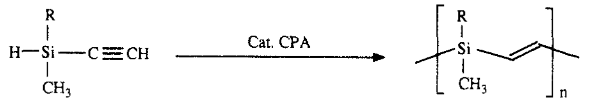
Methylphenylchlorosilane was condensed with chloromagnesium acetylide to give methylphenylethynylsilane (**4**). Polymerization was carried out by slow addition of **4** to a solution of CPA in THF at room temperature. The first few drops of **4** produced smooth reflux, which was continued until the addition was complete. After purification by precipitation with added methanol, yellowish glassy polymer **5** was obtained in ca. 95% yield. Polymer **5** had a molecular weight (M_W) of 11 400 and was soluble in common organic solvents such as THF, benzene, and CCl_4. Polymerization of dimethylethynylsilane (**6**) was

---

⊗ Abstract published in *Advance ACS Abstracts,* September 1, 1993.

0024-9297/93/2226-5671$04.00/0

Scheme III

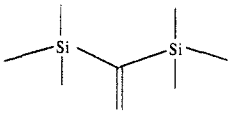


4 R = Ph THF, 95% yield 5 M_w = 11,400, M_w/M_n = 2.5
(neat) (M_w = 30,000, M_w/M_n = 4.8)

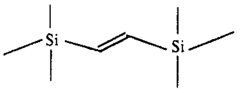
6 R = Me THF, 66% yield 3 M_w = 30,380, M_w/M_n = 4.8
(neat) (M_w = 85,000, M_w/M_n = 4.3)

also performed with catalytic CPA in THF to afford, after purification, silylene–alkene polymer 3 in 66% yield. Although CPA-catalyzed hydrosilylation of 4 and 6 produced polymers of higher molecular weight, use of a minimum amount of solvent in these reactions is essential since the neat polymerization can be violently exothermic and 6 is quite volatile (Scheme III). Polymer 3 was a white powder, soluble in organic solvents such as THF, toluene, methylene chloride, and CCl_4 and started to melt at 108 °C without decomposition.

Silylene–olefin polymers 3 and 5 could either be of the α,β- or α,α-type since, in reactions involving Si–H addition to an ethynyl group using CPA as a catalyst, a mixture of α- and β-isomers is often obtained, although the β-isomer always is predominant.[11]


α,α-isomer

or


α,β-isomer

The NMR spectra of both 3 and 5 are consistent only with a regular α,β-structure. For example, polymer 3 exhibits only one sharp resonance signal in its ^{29}Si NMR spectrum (Figure 1) and only one singlet vinyl carbon signal at ca. 150 ppm in its ^{13}C NMR spectrum (Figure 2). The abnormal downfield chemical shift of the vinyl carbon in the ^{13}C NMR spectrum is consistent with the literature value of the model system 1,2-bis(trimethylsilyl)ethylene (150.5 ppm).[12]

The fixed 1:1 ratio of functional groups in the hydridoethynylsilane monomers is very important to obtain high molecular weight polymers as shown in the following equation[13] for X_n, the number-average degree of polymerization:

$$X_n = (1 + r)/(1 + r - 2rp)$$

where p is the fraction of functionality converted during reaction and r = number of Si–H groups/number of –C≡CH groups.

X_n reaches a maximum when r equals unity. Changing reaction time or solvent (benzene or THF) did not affect the molecular weights of the final polymers. Analysis of the IR spectra of polymer 3 (Figure 3) and the corresponding monomer revealed that a small amount of excess acetylene (very weak absorptions at 2037 and 3294 cm^{-1}) was present in the polymer product. No residual Si–H was detected in the polymers by either IR or ^{1}H NMR.

These results suggest that the stoichiometric ratio (r) between Si–H and ethynyl groups was lost during the reaction, and the polymer end groups possess free acetylene units. This is most likely caused by CPA-catalyzed reaction of Si–H and any residual moisture in the reaction flask.[14] Another possible source of Si–H loss is hydrosilylation of the double bonds of the polymer main chain, which would produce some chain branching. Although evidence of such chain branching was not detectable by spectroscopic analysis, support for the possibility of its occurrence via hydrosilylation, albeit under far more extreme conditions, was found in the CPA-catalyzed polymerization of diethylethynylsilane (7), which required heating at 160 °C for 9 h for completion (Scheme IV).

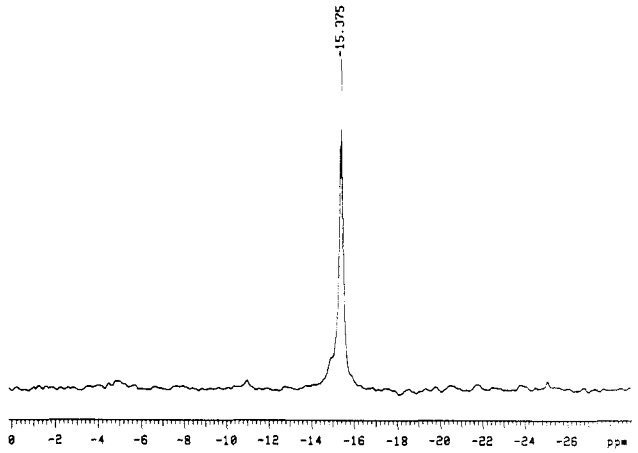


Figure 1. Gated decoupling ^{29}Si NMR of polymer 3.

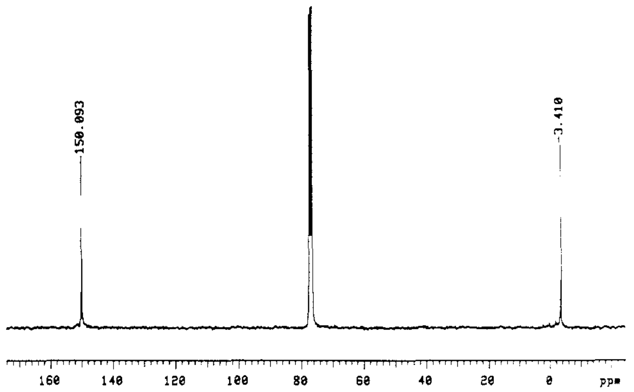


Figure 2. Gated decoupling ^{13}C NMR of polymer 3.

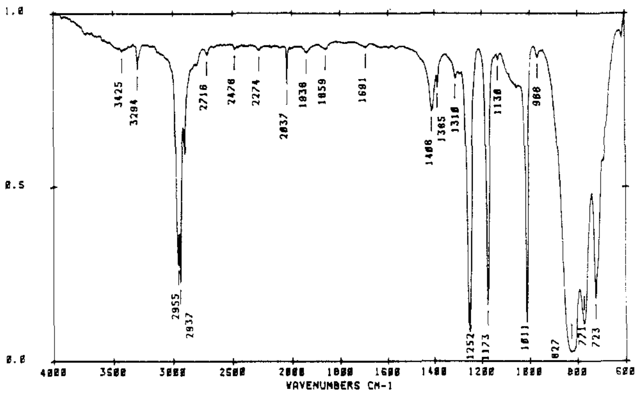
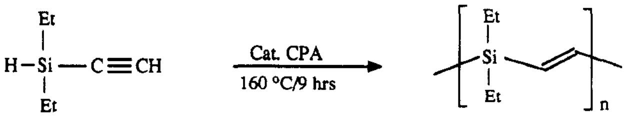


Figure 3. IR spectrum of polymer 3.

Scheme IV



7 8 M_w = 110,700

Polymer 8 was an elastic, sticky resin with a very broad, multimodal molecular weight distribution (PDI = 36).

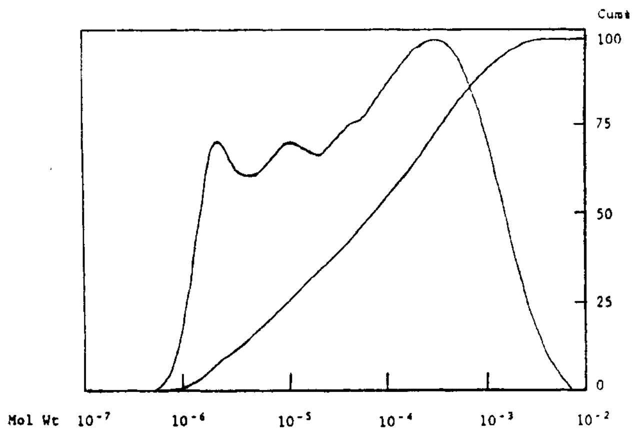


Figure 4. GPC chromatogram of polymer 8.

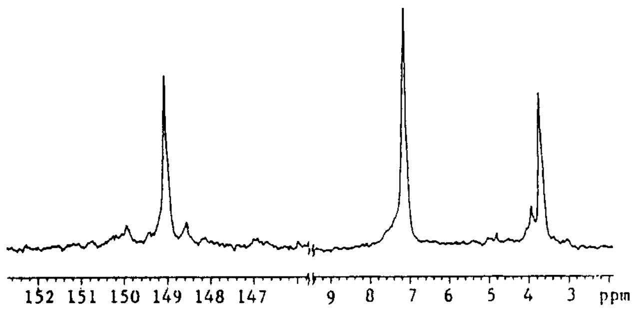


Figure 5. ^{13}C and ^1H NMR spectra of polymer 8.

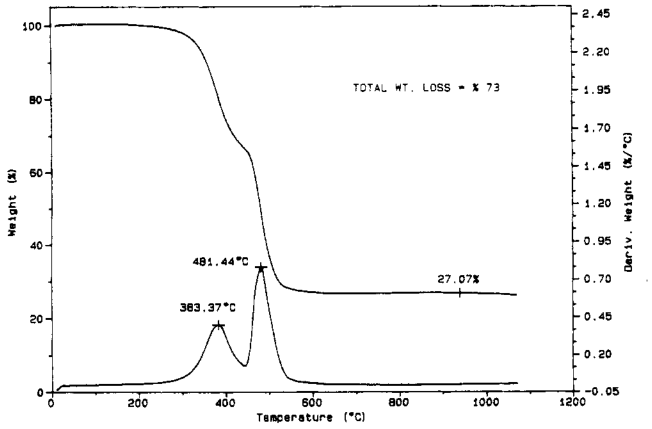


Figure 6. TGA curve of polymer 3.

Clearly, the steric bulk of the side group on the silicon atom plays an important role. Both the abnormally large PDI and the multimodal curve of the GPC chromatogram (Figure 4) strongly suggest that the polymer is branched. NMR (^1H and ^{13}C) analysis of polymer 8 revealed it to have largely the regular structure shown in Scheme IV; however, the weak signals at 148.6 and 150 ppm in the ^{13}C NMR spectrum (Figure 5) may be associated with the branched structure.

Thermal degradation of polymers 3, 5, and 8 was investigated by thermogravimetric analysis (TGA) in a helium atmosphere (Figures 6–8). Decomposition started at ca. 300 °C and the maximum rates of decomposition were between 450 and 500 °C, significantly lower than for the corresponding silylene–acetylene polymers,[7a,15] where the maximum rate of decomposition was reached at ca. 550–650 °C. The volatile products of the polymer pyrolyses were analyzed in a separate system composed of a vacuum pyrolysis tube connected to a quadrupole mass spectrometer either directly or via a gas chromatograph. The condensable decomposition components were collected by a cold finger trap and then analyzed by GC–MS, GC–FTIR, and NMR.

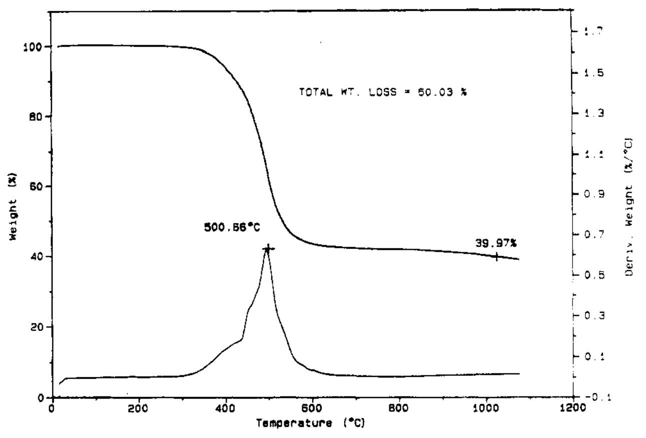


Figure 7. TGA curve of polymer 5.

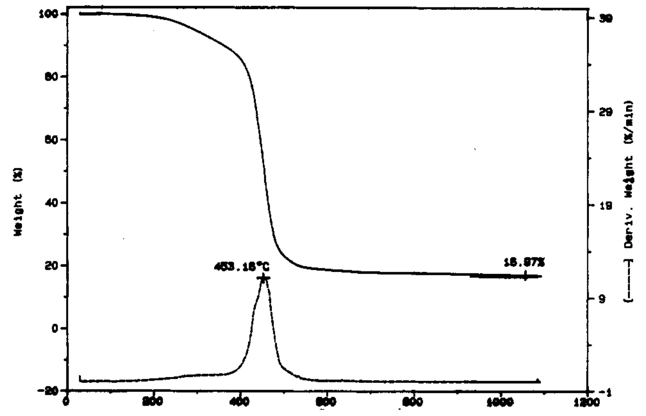


Figure 8. TGA curve of polymer 8.

Pyrolysis of dimethylsilvinylene polymer 3 exhibited unusual behavior in that the char yields were not reproducible and varied from 15 to 42% (theoretical for SiC is 47.6%). Mass spectral analysis revealed that several silicon-containing products were among the many uncharacterized compounds in the complex mixture of condensed products.

Methane was the only volatile (not condensed at −78 °C) product of thermal degradation of phenylmethylsilvinylene polymer 5 up to 500 °C, but at higher temperatures hydrogen is evolved. Analysis of the condensed pyrolysis products from 5 at 450–550 °C showed 54% benzene, 14% toluene, 6% ethylbenzene, 13% dimethylphenysilane, and some minor uncharacterized products.

Thermal decomposition of diethylsilvinylene polymer 8 started to produce ethylene as low as 200 °C. From 200 to 600 °C only ethylene (major), ethane (minor), and some hydrogen (only at 600 °C) were detected as gaseous products. The char yield, however, was only ca. 17% (theoretical 35.7%), due to oligomer formation and volatilization during pyrolysis.

The nonvolatile chars obtained after pyrolysis of polymers 3, 5, and 8 were black and were oxidative stable at 1200 °C in air. X-ray powder diffraction revealed only β-SiC.

Polymer 5 (but not 3 or 8) can be pulled into very long (>100 cm) flexible fibers from its melt. Surface cross-linking of the polymer fiber is conveniently accomplished by exposure to UV light (low-pressure mercury arc lamp). Cross-linking proceeds in inert gas as well as in air. Cross-linked polymer fibers were pyrolyzed under a helium flow at 1100 °C to yield ceramic fibers. An SEM micrograph of a pyrolyzed fiber from polymer 5 is shown in Figure 9.

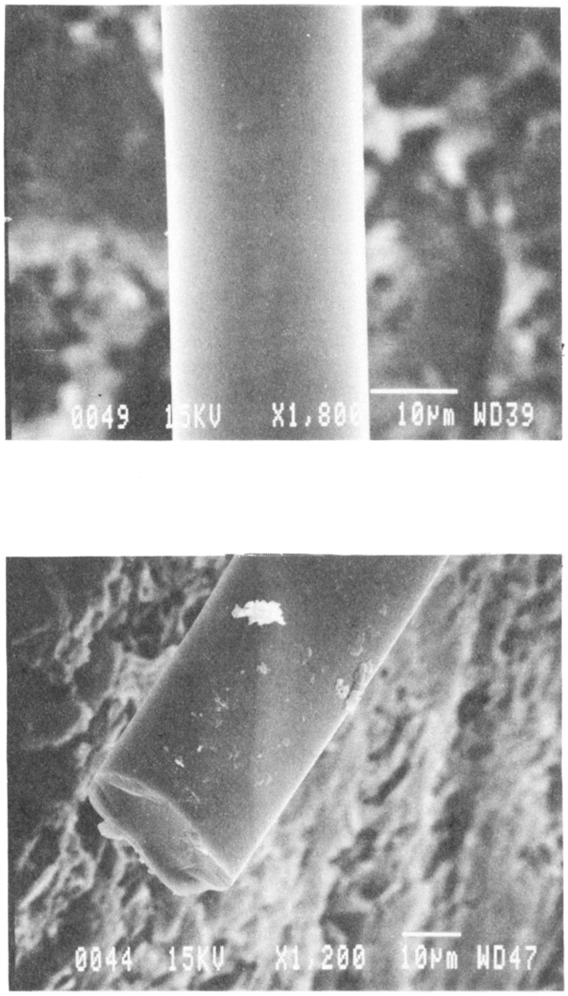


Figure 9. SEM micrograph of ceramic fiber from polymer **5**.

Experimental Section

Instrumentation. Infrared spectra were obtained from KBr pellets and recorded on an IBM Model IR/98 FTIR. ^{1}H NMR, ^{13}C NMR, and ^{29}Si NMR were obtained from $CDCl_3$ solutions and recorded on a Varian VXR 300. Molecular weights were determined by GPC with retention times calibrated against nine narrow-dispersity polystyrene samples (Polymer Labs). GPC analyses were performed on a Perkin-Elmer Series 601 liquid chromatograph equipped with a Waters Associates R401 RI detector and a Nelson analytical data system. Five μ-Styragel columns (10^6, 10^5, 10^4, 10^3, 500 Å) were employed in series with a THF flow rate of 1 mL/min. Thermogravimetric analyses (TGA) were performed on a DuPont Model 951 thermal analyzer. Combustion analyses were performed on a HORIBA EMIA-520 carbon-analysis instrument. Polymer pyrolysis was done in a graphite crucible placed into a heated quartz tube which was interfaced either directly to a VG SX300 quadrupole mass spectrometer or via a Varian 6000 gas chromatograph. Mass spectra were obtained on a Hewlett-Packard Model 5970 GC–MS and are reported as m/z (percent relative ion intensity).

Ethynylmagnesium chloride was prepared from methylmagnesium chloride and acetylene in anhydrous THF according to the procedure of Holmes and Spoyikou.[16]

Preparation of Ethynylmethylphenylsilane (4). Ethynylmagnesium chloride (0.16 mol in 200 mL of THF) was prepared in a 500-mL oven-dried, round-bottomed, three-necked flask, equipped with a magnetic stirring bar and a graduated pressure-equalizing addition funnel.[16] After the solution was cooled to −78 °C, phenylmethylchlorosilane (25 g, 0.16 mol, Petrarch) was added dropwise. After completion of addition, the reaction mixture was allowed to gradually warm to room temperature and then stirred for 2 h. After the reaction mixture was cooled in an ice-water bath, 100 mL of hexane and 100 mL of cold, dilute aqueous HCl solution were added. The organic layer was separated and dried over anhydrous Na_2SO_4, and the majority of the solvent was removed by rotatory vacuum evaporation. Fractional distillation through a 5-cm helices-packed column afforded **4**[17] as a colorless liquid (21.3 g, yield 92%), bp 70–72 °C/13 mmHg, purity 98% by GC. **4**: mass spectrum 147 (12, $M^+ + 1$), 146 (65, M^+), 145 (100, $M^+ - H$), 132 (14), 131 (91, $M^+ - Me$), 120 (23), 105 (61), 77 (20), 68 (47, $M^+ - Ph$); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.52 (d, J = 3.9 Hz, 3 H), 2.55 (s, 1 H), 4.65 (q, J = 3.9 Hz, 1 H), 7.30–7.75 (m, 5 H); IR (neat) ν 3231 (s), 3071 (m), 2913 (w), 2149 (s), 2039 (s), 1429 (s), 1254 (s), 1117 (s), 991 (vs), 937 (vs), 749 (s), 725 (s), 600 (m) cm^{-1}.

***Warning*:** *Catalytic hydrosilylation reactions are quite exothermic. It is strongly advised that solvent (THF) be used for thermal moderation and that the usual safety precautions of safety shields and eye protection be employed for the following procedures.*

Polymerization of Ethynylmethylphenylsilane (4). A catalytic amount (ca. 1 mg) of H_2PtCl_6 was dissolved in ca. 2 mL of anhydrous THF in a 25-mL oven-dried, round-bottomed flask equipped with a condenser and a magnetic stirring bar. The solution was heated at 50 °C, and phenylmethylethynylsilane (4 mL, 3.2 g) was added dropwise. The reaction was exothermic and the solution became more and more viscous until the polymerization was complete. After the reaction subsided, the condenser was removed and the flask was fitted with a short-path distillation apparatus. The solvent was distilled and the viscous remains were heated at 120 °C overnight. After cooling to room temperature, a pale-yellow, transparent resin was obtained. GPC analysis of a THF solution of the resin showed M_W = 11 410, PDI = 2.5. **5**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ −0.1–0.8 (broad peak, 3 H), 6.7–6.9 (broad, 1 H), 7.0–7.9 (broad, 5 H); ^{13}C NMR ($CDCl_3$, 75.429 MHz) δ 150.2 (1 C), 136.6 (1 C), 134.5 (2 C), 129.1 (1 C), 127.8 (2 C), −4.7 (1 C); ^{29}Si NMR ($CDCl_3$, 59.595 MHz) δ −19.3; IR (KBr pellet) ν 3271 (vw), 3067 (m), 3009 (m), 2035 (vw), 1427 (s), 1250 (s), 1173 (s), 1109 (s), 1013 (s), 791 (s), 733 (s), 696 (s), 471 (m) cm^{-1}. The carbon content of the char from heating **5** to 1100 °C was 74.4%.

Preparation of Dimethylethynylsilane (6). Ethynylmagnesium chloride (0.5 mol) was prepared[16] in 300 mL of THF in a 1000-mL oven-dried, three-necked flask. To this solution was added dimethylchlorosilane (54 mL, 0.5 mol) dropwise at −78 °C. After completion of addition, the mixture was gradually warmed to room temperature, capped with a balloon, and stirred for 2 h before cooling to 0 °C by an ice-water bath. Dilute, cold aqueous HCl solution (0.2 M, 200 mL) was added, the mixture was poured into a separation funnel, and the organic layer was separated. After drying over anhydrous sodium sulfate, the solution was distilled through a 25-cm helices-packed column into a dry ice cooled receiver flask. Dimethylethynylsilane[18] (**6**), a colorless liquid (ca. 36 g, 85% yield, 94.5% pure by GC), was collected below 40 °C. **6**: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.13 (heptet, J = 3.78 Hz, 1 H), 0.27 (d, J = 3.86 Hz, 6 H), 2.4 (s, 1 H); mass spectrum 84 (21, M^+), 83 (27, $M^+ - 1$), 69 (100, $M^+ - Me$).

Polymerization of Dimethylethynylsilane (6). A catalytic amount (ca. 1 mg) of H_2PtCl_6 was dissolved in 5 mL of THF in a 50-mL flask equipped with a cold finger filled with dry ice and 2-propanal. Dimethylethynylsilane (**6**) (10 mL) was added dropwise via syringe at a rate sufficient to maintain a gentle reflux. The mixture was stirred overnight. After precipitation by addition of methanol (50 mL), polymer **3**, a white solid (4.2 g, 66%) with a softening point of ca. 95–105 °C, was removed by filtration. **3**: GPC M_W = 30 381, PDI = 4.82; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.12 (s, 2 H), 6.59 (s, 6 H); ^{13}C NMR ($CDCl_3$, 75.429 MHz) δ −3.41 (2 C), 150.09 (2 C); ^{29}Si NMR ($CDCl_3$, 59.595 MHz) δ −15.37. The carbon content of the char from heating **3** to 1100 °C was 39.8%.

Synthesis of Diethylchlorosilane. An oven-dried 2-L flask equipped with a magnetic stirring bar and addition funnel was charged with freshly distilled trichlorosilane (80.7 mL, 0.8 mol) and anhydrous diethyl ether (700 mL). The solution was cooled to −78 °C, and ethylmagnesium chloride (1.6 mol in 800 mL of Et_2O, Aldrich) was added dropwise while efficient stirring was maintained. After completion of addition, the mixture was stirred at −78 °C for 1 h and then gradually warmed to room temperature overnight. Most of the salts were removed by filtration of the reaction product mixture through a sintered glass filter. Distillation through a 25-cm column packed with glass helices gave diethylchlorosilane[19] as a colorless liquid (90 g, 90% pure by GC, yield 83%): bp 100–101 °C; GC–MS 124 (3.7, $M^+ + 2$), 123 (5.3, $M^+ + 1$), 122 (11.1, M^+), 121 (13.5), 95 (33.6), 94 (22.3), 93 (100, $M^+ - C_2H_5$), 92 (46.2), 67 (15.9), 65 (53.2), 63 (23.5).

Synthesis of Ethynyldiethylsilane (7). Ethynylmagnesium chloride (0.7 mol) was prepared[16] from methylmagnesium chloride (0.7 mol) and acetylene in 900 mL of anhydrous THF in a 2-L oven-dried, three-necked, round-bottomed flask equipped with a magnetic stirrer, a gas inlet, and a gas outlet. After the ethynylmagnesium chloride solution was cooled to −78 °C, diethylchlorosilane (90 g, 90% pure) was added dropwise through an addition funnel. After addition, the mixture was stirred at −78 °C for 20 min, then gradually warmed to room temperature, and stirred overnight. Another 2-L flask equipped with a magnetic stirring bar and cooled by an ice bath was charged with 300 mL of dilute aqueous HCl and 200 mL of pentane. Into this mixture the above product solution was slowly added in portions. The organic layer was separated, washed once with cold, dilute aqueous HCl, and dried over Na_2SO_4. Fractional distillation through a 45-cm column packed with glass helices gave 25 g (34% yield) of 7[20] as a colorless liquid, bp 98.5–99 °C/760 mmHg. The low yield was due to difficulty in separating the impurities of similar boiling point, e.g., triethylsilane (bp 107–108 °C) and ethyldiethynylsilane. The product was 97% pure by GC, with the remainder being 1.4% ethyldiethynylsilane and 1.6% triethylsilane. This product was used in the following polymerization studies. 7: mass spectrum 112 (1.2, M^+), 111 (3.0, $M^+ - H$), 84 (22, $M - C_2H_4$), 83 (62.5, M − Et), 82 (11.4), 81 (18), 67 (10), 58 (11), 57 (10), 56 (12). 55 (100); IR (neat) ν 3307 (m), 2970 (m), 2179 (s), 2043 (m), 1344 (m), 973 (w), 818 (vs) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.93 (dq, $J_1 = 3.6$ Hz, $J_2 = 0.9$ Hz, 1 H), 2.39 (d, $J = 0.9$ Hz, 1 H), 1.04 (t, $J = 7.8$ Hz, 6 H), 0.70 (dq, $J_1 = 7.8$ Hz, $J_2 = 3.3$ Hz, 4 H).

Polymerization of Ethynyldiethylsilane (7) in the Presence of Chloroplatinic Acid. A catalytic amount (ca. 1 mg) of chloroplatinic acid was dissolved in 0.2 mL of anhydrous THF in a 25-mL oven-dried, round-bottomed flask equipped with a magnetic stirring bar and a condenser. Monomer 7 (5 mL, 3.82 g) was added dropwise via syringe. Heating this mixture in an oil bath at 120 °C for 6 h only slightly increased the viscosity. After the mixture was heated at 160 °C for 9 h, polymer 8 was formed as a sticky, elastic resin which was readily soluble in THF, $CHCl_3$, and toluene. 8: GPC $M_W = 110\,700$, PDI = 36; ^1H NMR ($CDCl_3$, 300 MHz) δ 6.598 (s, 1.727 H), 6.395 (s, 0.273 H), 0.921 (t, $J = 7.8$ Hz, 6 H), 0.635 (q, $J = 7.8$ Hz, 4 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.429 MHz) δ 149.06, 7.15, 3.75. The carbon content of the char from heating 8 to 1100 °C was 54.7%.

Acknowledgment. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences.

References and Notes

(1) Baney, R. H.; Chandra, G. In *Encyclopedia of Polymer Science and Engineering*; John Wiley and Sons: New York, 1988; pp 13, 312.

(2) Yajima, S. *Am. Ceram. Soc. Bull.* **1983**, *62*, 893.

(3) Carlsson, D. J.; Cooney, J. D.; Gauthier, S.; Worsfold, J. D. *J. Am. Ceram. Soc.* **1990**, *73* (2), 237.

(4) Bacque, E.; Pillot, J. P.; Birot, M.; Dunogues, J. *Macromolecules* **1988**, *21*, 30.

(5) Bacque, E.; Pillot, J. P.; Birot, M.; Dunogues, J. *Macromolecules* **1988**, *21*, 34.

(6) Wu, H.-J.; Interrante, L. V. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1991**, *32* (3), 588; *Macromolecules* **1992**, *25*, 1840.

(7) (a) Ijadi-Maghsoodi, S.; Pang, Y.; Barton T. J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 955. (b) Iwahaya, T.; Hayase, S.; West, R. *Macromolecules* **1990**, *23*, 1298. (c) Ishikawa, M.; Hatano, T.; Hasegawa, Y.; Horio, T.; Kunai, A.; Miyai, A.; Ishida, T.; Tsukihara, T.; Yamanaka, T.; Koike, T.; Shioya, J. *Organometallics* **1992**, *11*, 1604. (d) Ishikawa, M.; Hasegawa, Y.; Hatano, T.; Kunai, A. *Organometallics* **1989**, *8*, 2744. (e) Seyferth, D.; Wiseman, G. H.; Targos, T. S.; Sabon, C. A.; Wood, T. G.; Koppetsch, G. E. *Silicon Chemistry*; Ellis Horwood Ltd.: Chichester, England, 1988; Chapter 38, p 415.

(8) Korshak, V. V.; Sladkov, A. M.; Luneva, L. K. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* **1962**, 2251.

(9) Luneva, L. K.; Sladkov, A. M.; Korshak, V. V. *Vysokomol. Soedin.* **1965**, *7* (3), 427.

(10) Andrianov, K. A.; Pakhomov, V. M.; Gel'perina, V. M.; Semenova, G. A. *Vysokomol. Soedin.* **1966**, *8* (9), 1623.

(11) Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. *J. Organomet. Chem. Library* **1977**, *5*, 1.

(12) Sakurai, H.; Tobita, H.; Nakadaira, Y. *Chem. Lett.* **1982**, *8*, 1251.

(13) Odian, G. *Principles of Polymerizaton*, 2nd ed.; John Wiley and Sons: New York, 1981: p 83.

(14) Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

(15) Ijadi-Maghsoodi, S.; Zhang, X.; Pang, Y.; Meyer, M.; Akinc, M.; Barton, T. J. *Polym. Prep.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1991**, *32*, 577.

(16) Holmes, A. B.; Sporikou, C. N. *Org. Synth.* **1987**, *65*, 61.

(17) Kraihanzel, C. S.; Losee, M. L. *J. Organomet. Chem.* **1967**, *10*, 427.

(18) Bakassian, G.; Lefort, M. German Patent 2,146,416, May 25, 1972; *Chem. Abstr.* **1972**, *77*, 88663S.

(19) Sergeeva, Z. I.; Tszyan-Ian, S. *Zh. Obshch. Khim.* **1963**, *33* (6), 1874.

(20) Komarov, N. V.; Yarosh, O. G. *Zh. Obshch. Khim.* **1967**, *37*, 264.