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Preparation of a Polymeric Precursor to Silicon Carbide via Ring-Opening Polymerization: Synthesis of Poly[(methylchlorosilylene)methylene] and Poly(silapropylene)

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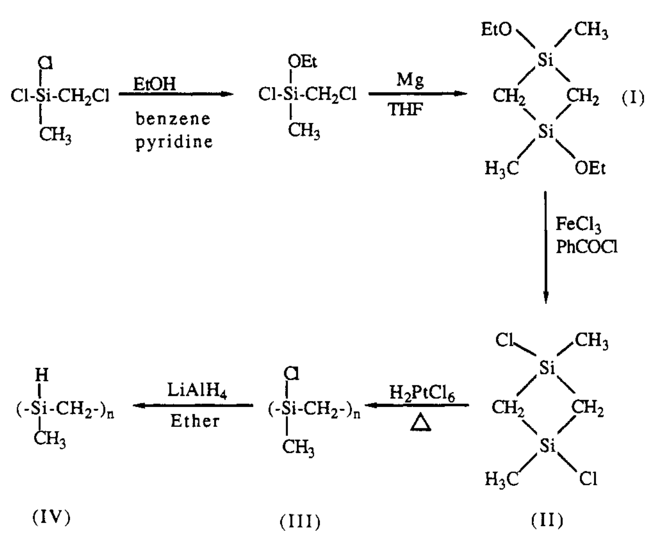
A high molecular weight linear polycarbosilane, poly[(methylchlorosilylene)methylene], $[-(CH_3)SiClCH_2-]_n$, has been prepared by ring-opening polymerization of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane. Reduction of this polymer with $LiAlH_4$ yields the corresponding polysilapropylene, $[-(CH_3)SiHCH_2-]_n$. The structures of these polymers and their monomeric precursors have been investigated by IR and ^1H, ^{13}C, and ^{29}Si NMR spectroscopy, mass spectra, and GPC. The results of these studies are consistent, in the case of the polymers, with expectations for high molecular weight linear polymers with atactic configurations. The pyrolysis of the high molecular weight poly(silapropylene) was studied by TGA and was found to give a 66% ceramic yield after thermal processing at 400 °C, suggesting that this polymer has potential for use as a precursor to SiC ceramics.

Introduction

Since the development of Nicalon SiC fiber, following the pioneering work of Yajima in Japan,[1] there has been continued interest in the development of new sources of SiC fiber with improved high-temperature properties. A persistent problem in this area has been the difficulty of obtaining a high molecular weight polymer that will have the requisite physical properties for fiber spinning along with a high ceramic yield of stoichiometric SiC. Most prior efforts have focused on polysilanes as SiC precursors, presuming, with good justification, that linear polycarbosilanes are subject to depolymerization on pyrolysis.[2] Indeed, all previous studies of linear polycarbosilanes have evidenced considerable loss of Si and C on heating to 1000 °C, often resulting in ceramic yields close to zero. However, the polycarbosilanes that have been studied either are low molecular weight polymers or have only inert groups such as methyl as the substituents on Si.[3,4] In this paper we report the use of ring-opening polymerization to prepare a high molecular weight polycarbosilane with improved physical properties and ceramic yield.

The ring-opening polymerization of various derivatives of 1,3-disilacyclobutane has been conducted using a variety of catalysts;[5-9] however the application of this method to prepare polymeric precursors to SiC has not been pursued until recently. Smith and Rouge claimed that with 1,3-disilacyclobutane as the monomer they were able to make a linear polymer that gave a 85% ceramic yield.[10] Since the Si–H bond also is activated by the transition-metal catalyst they used, it seems doubtful that a linear polymer has been formed.[2] Donogues and co-workers used this approach to prepare a high molecular weight (M_n = 250 000) linear poly[(dimethylsilylene)methylene], which they converted to poly[(methylchlorosilylene)methylene] by treatment with trimethylchlorosilane in the presence of aluminum chloride.[4] However, during this conversion, they also cleaved $Si-CH_2-Si$ bonds and reduced the molecular weight to 2300. The derived poly(silapropylene) was found to give extremely poor ceramic yields. Therefore a well-characterized polycarbosilane that exhibits high molecular weight and high ceramic yield remains as a desirable objective.

Scheme I



We describe here the results of efforts to employ 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane as a monomer for the preparation of a polycarbosilane by ring-opening polymerization as shown in Scheme I. Through the activity of the Si–Cl bond, we obtain the ability to introduce various substituents into the polymer, allowing modifica-

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tion of the properties of the polymer as well as improvement in the ceramic yield.

Experimental Section

General Comments. All manipulations were carried out in oven-dried glassware under nitrogen following standard inert-atmosphere techniques.[11] All solvents were distilled from appropriate drying agents under a nitrogen atmosphere prior to use.[12] The reagents employed were available commercially unless otherwise indicated. NMR spectra were obtained by using a Varian XL-200 NMR spectrometer with benzene-d_6 used as solvent and internal standard. IR spectra were obtained by using a Perkin-Elmer 298 infrared spectrophotometer. Mass spectra were recorded on a Varian Mat 731 spectrometer (chemical ionization). Molecular weights of the polymers were determined by GPC by using a Waters 600 multisolvent delivery system and a Waters 745 data module with three μ-Styragel columns (porosity ranges of 100, 500, 10 000 Å) calibrated with polystyrene standards and with toluene as the eluent at a flow rate of 0.6 mL/min. The detection system used was a Waters 410 differential refractometer. TGA studies were carried out by using a Perkin-Elmer TGA 7 thermogravimetric analyzer with a heating rate of 10 °C/min under nitrogen. Elemental analyses were carried out by Galbraith Laboratories, Inc.

Preparation of 1,3-Diethoxy-1,3-dimethyl-1,3-disilacyclobutane. The compound 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane (I) was prepared in 30% yield by a Grignard reaction from (chloromethyl)methylethoxychlorosilane as described by Kriner;[14] IR 2975 s, 2935 m, 2900 m, 2880 m, 1485 w, 1445 w, 1390 m, 1340 m, 1290 w, 1250 s, 1165 ms, 1105 vs, 1075 vs, 950 vs, 840 vs, 795 s, 765 s, 700 m cm^{-1}; ^{1}H NMR (C_6D_6 solution) δ 3.6 (doublet of quartets, 2 H, OCH_2CH_3), 1.11 (doublet of triplets, 3 H, OCH_2CH_3), 0.46 (2 H, $SiCH_2Si$), 0.27 (doublet, 3 H, CH_3); ^{13}C NMR (C_6D_6 solution) δ 5.65 (doublet, $OCH_2C^*H_3$), 18.66 ($OC^*H_2CH_3$), 8.6 ($SiCH_2Si$), 1.25 (doublet, $SiCH_3$); ^{29}Si NMR (C_6D_6 solution) δ 8.18, 5.63; MS (CI), *m/e* (rel intensity, ion), 159 (4%, M − 45), 177 (5%, M − 27), 205 (100%, M + 1).

Preparation of 1,3-Dichloro-1,3-dimethyl-1,3-disilacyclobutane. Preparation of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane (II) followed the method described by Kriner;[14] IR 2985 m, 2900 w, 1390 m, 1340 s, 1255 s, 955 vs, 920 m, 865 s, 845 s, 800 vs, 770 vs, 715 s, 690 s, 650 s, 615 vs cm^{-1}; ^{1}H NMR (C_6D_6 solution) δ 0.799 (2 H, $SiCH_2Si$), 0.397 (3 H, CH_3); ^{13}C NMR (C_6D_6 solution) δ 15.48 (doublet, $SiCH_2Si$), 4.13 (doublet, CH_3); ^{29}Si NMR (C_6D_6 solution) δ 23.13, 22.18.

Ring-Opening Polymerization of 1,3-Dichloro-1,3-dimethyl-1,3-disilacyclobutane. Chloroplatinic acid (0.016 g, 0.008 g in second attempt) was added to 2 g of II in a 50-mL three-necked flask equipped with a magnetic stir bar. This mixture was heated with an oil bath at 80 °C for 16 h. A viscous brown polymer was obtained which was used directly in the following reactions without further purification.

Reduction of Poly[(methylchlorosilylene)methylene]. The polymer obtained from the previous reaction was dissolved in 20 mL of ethyl ether. A mixture of 0.3 g of $LiAlH_4$ in 20 mL of ethyl ether was added slowly to the polymer solution via syringe with proper stirring. After all the $LiAlH_4$ was added, the solution was left at room temperature to stir overnight. A solution of 3 M hydrochloric acid then was added slowly until two layers were observed. The ether layer was removed and evaporated under vacuum to yield a yellow viscous polymer. The polymer was dissolved in 20 mL of pentane, filtered, and recovered by evaporation of the pentane under vacuum, yielding 1.2 g of a yellow, extremely viscous polymer (yield >95%, based on II). Elemental analysis: Si, 43.8%; C, 41.38%; H, 9.04% (calculated: Si, 48.28%; C, 40.64%; H, 9.04%).[13]

Ring-Opening Polymerization of 1,1,3,3-Tetramethyl-1,3-disilacyclobutane (V). The preparation of V followed the procedure described by Kriner.[14] Its polymerization in the absence of solvent was carried out as described out as described by Bacque.[4] The polymerizations that were carried out in hexane or benzene employed the same procedure except that a solution of 1:3 V to solvent (based on volume) was used in the solution polymerization. The solution was refluxed for 24 h to effect polymerization. In either case a viscous yellow polymer (VI) was obtained after purification by dissolution in hexane followed by filtration and removal of hexane under vacuum.

Heat Treatment of Poly(silapropylene). Poly(silapropylene), (0.5 g) was placed in a 5-mL Kimax test tube that was connected via a rubber septum and cannula tube to a silicone oil bubbler tube under nitrogen. The polymer was heated in the test tube slowly from 120 to 400 °C in 30 min and held at 400 °C for 5 min. It was then cooled to room temperature, yielding a hard rubbery polymer.

Results and Discussion

Our initial work focused on the ring-opening polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane, following the procedure described by Kriner. A linear polymer, poly[(dimethylsilylene)methylene], of high molecular weight (M_n = 260 000, polydispersion index = 1.45) was obtained. However, due to the inertness of the Si–Me bond, this polymer is thermally stable up to 450 °C under nitrogen (3% weight loss) and then decomposes rapidly between 450 and 550 °C to give a negligible ceramic yield. Therefore, even though this polymer has a high molecular weight, without proper functionality it cannot cross-link and, instead, depolymerizes to give volatiles under pyrolysis. Since the cleavage of $Si–CH_3$ bonds will inevitably also cleave the $Si–CH_2–Si$ chain and reduce the molecular weight,[4] we chose to introduce functionality onto the main chain of the polymer. The Si–Cl bond provides a convenient entry point for further functionalization of the polymer while resisting attack under the conditions of the ring-opening polymerization.

The direct synthesis of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane via Grignard reaction of (chloromethyl)dichloromethylsilane is reported to yield a variety of cyclic and polymeric carbosilanes with a very small amount of the desired four-membered-ring compound.[14] This was confirmed in our attempt to repeat this synthesis. Again, following the work of Kriner,[14] much higher yields of this monomer are afforded through the use of ethoxy as a protecting group on Si during the Grignard reaction.

Synthesis of the Monomers. The ^{1}H, ^{13}C, and ^{29}Si NMR spectra of both the ethoxy-substituted I and chloro-substituted II cyclic oligomers show twice the number of peaks expected for the individual cis or trans isomers, indicating the coexistence of these two isomers in the samples we have obtained. Since the Grignard reaction is not reversible, the formation of cis and trans isomers depends on the configuration of the reagent as it forms the ring. From the NMR spectra, the ratio of cis to trans isomers is 1:1, which indicates that there is no strong preference for either one.

In the procedure involving the reverse addition of magnesium powder, the composition of the Grignard reaction products is affected greatly by the rate of addition of magnesium powder. In our first attempt, 7 g of magnesium powder was added to the reactant over 1 h, and we obtained only a 15% yield of I. The procedure was then repeated with a reduced addition rate (14 g in 4 h), giving a 30% yield of I. The other products of this reaction are mainly linear oligomers (45% yield) of the type (–SiO-

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[11] Shriver, D. F.; Drezdzon, M. A. *Manipulation of Air Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

[12] Gordon, A. J.; Ford, R. A. *The Chemist's Companion*; Wiley: New York, 1977.

[13] The total of the elemental analysis is less than 100%, due to the low value obtained for Si. Similar low Si values have been reported for carbosilanes and have been attributed to incomplete combustion of the compound. See ref 4. Baney, H. R.; Gaul, J. H.; Hilty, T. K. *Organometallics* **1983**, *2*, 859. Patai, S., Rappoport, Z., Eds. *The Chemistry of Organic Silicon Compounds*; Wiley: New York, 1989; Chapter 6.

[14] Kriner, W. A. *J. Org. Chem.* **1964**, *29*, 1601.

Table I. Infrared Absorption Spectrum for Poly[(chloromethylsilylene)methylene]

wave-number, cm^{-1}	assignment	wave-number, cm^{-1}	assignment
2965 (m)	CH_3 stretch	1260 (s)	CH_3–Si deformation
2900 (w)	CH_2 stretch	1060 (vs)	Si–CH_2–Si deformation
2880 (w)	CH_3 stretch	810 (vs), 750 (s)	Si–CH_3 rocking
1410 (m)	CH_3–Si deformation	720 (m), 660 (m)	Si–C stretch
1350 (m)	Si–CH_2–Si deformation		

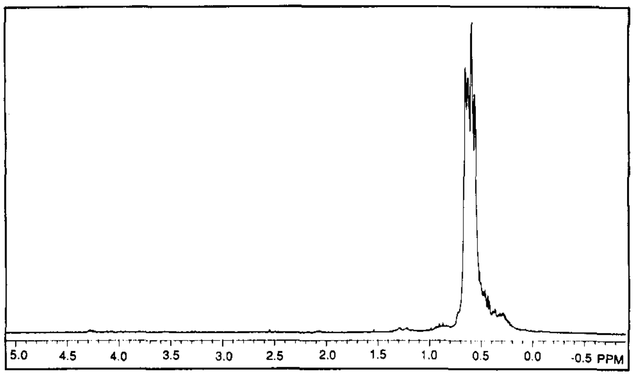

Figure 1. ^1H NMR spectrum of poly[(chloromethylsilylene)-methylene].

$EtMeCH_2-)_n$ with molecular weights that ranged from 2000 to 500 (M_n = 700), along with a 10% yield of the six-membered ring. This result is similar to that obtained from the reverse addition of magnesium powder to (chloromethyl)chlorodimethylsilane since both compounds have only one reactive functionality on Si (Cl) and can avoid the side reactions that lead to the variety of branched oligomeric products observed for the (chloromethyl)dichloromethylsilane.

Synthesis and Characterization of the Polycarbosilanes. After mixing the chloroplatinic acid with (II) and heating to 80 °C, we observed a gradual increase in the viscosity of the mixture; after about 10 min the mixture became so viscous that the magnetic stirrer could not rotate. This is to be contrasted with the finding of Kriner in his attempt of the same reaction, where "an oily product" was obtained,[9] suggesting a much lower molecular weight polymer than the one that we have obtained. The IR spectrum of this polymer (Table I) is the same as reported by Bacque.[4]

The ^1H NMR spectrum of this polymer is shown in Figure 1. The complex multiplet observed in this spectrum near 0.6 ppm is attributed to configurational effects in the polymer structure. Both "ionic polymerization" and "insertion–ring opening–propagation" pathways have been suggested for the ring-opening polymerization of disilacyclobutanes;[9,15] however, there is insufficient experimental evidence to permit a choice between these or other possible mechanisms. Regardless of the actual mechanism, with the coexistence of the cis and trans isomers, the likelihood of an atactic configuration for the polycarbosilane that we have prepared seems high. An analysis of the NMR spectra of both the chloro and hydrido polymers is consistent with this conclusion. A similar conclusion was reached by Bacque et al. in their study of the analogous polymers obtained by ring-opening polymerization of the symmetrical tetramethyldisilacyclobutane, followed by cleavage of methyl using trimethylchlorosilane in the presence of aluminum chloride and, finally, reduction with $LiAlH_4$.[4] Due to the large difference in both the preparation method and the molecular weight observed, a detailed analysis of the structure of the polymers that we have obtained seems warranted.

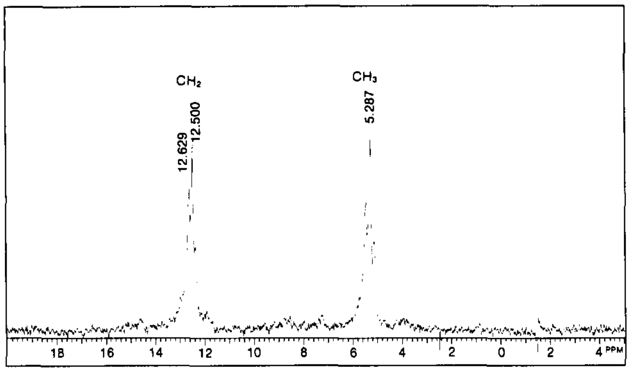

Figure 2. ^{13}C NMR spectrum of poly[(chloromethylsilylene)-methylene].

Table II. Infrared Absorption Spectrum for Poly(silapropylene)

wave-number, cm^{-1}	assignment	wave-number, cm^{-1}	assignment
2950 (m)	CH_3 stretch	1350 (w)	Si–CH_2–Si deformation
2900 (w)	CH_2 stretch		
2865 (w)	CH_3 stretch	1250 (s)	Si–CH_3 deformation
2100 (vs)	Si–H stretch		
1400 (w)	Si–CH_3 deformation	1070 (vs)	Si–CH_2–Si deformation
		880 (vs), 850 (vs)	Si–H bending
		780 (vs)	Si–C stretch

The interpretation of the NMR spectra of these polymers is aided by their analogy to the corresponding α-substituted vinyl polymers of the type $[-CRHCH_2-]_n$, whose structures have been extensively studied by using high-resolution NMR techniques.[16] Due to the different configurational sequences, a diad effect is observed for the $-CH_2-$ protons and a triad effect for the R = CH_3 protons, yielding two peaks for the former and three peaks for the latter. Further splitting of these peaks due to longer range interactions has also been observed in certain cases. In the case of poly[(methylchlorosilylene)methylene], due to the similar chemical shifts of the methyl and methylene protons, diad and triad effects are not observed clearly. This configurational effect can be more clearly seen in the ^{13}C NMR spectrum due to the larger chemical shift. The ^{13}C NMR spectrum shown in Figure 2 shows the expected triplet for the methyl carbon, which is the same as reported by Bacque.[4] However, the triplet observed for the methylene carbon would not be expected if only the diad effect is considered. This may suggest that longer range effects are operative in this case.

The ^{29}Si NMR spectrum, however, does not behave analogously to the corresponding methine carbon in the α-substituted vinyl polymers; as was reported by Bacque et al.,[4] only a single peak at 25.7 ppm vs TMS is observed. No signals attributable to terminal or branched carbon or silicon were observed for this polymer. No evidence for any head-to-head sequences were obtained either. All these spectra suggest that we have obtained the high molecular weight linear polymer, poly[(chloromethylsilylene)methylene], with no observable branching or head-to-head sequences.

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(15) Cundy, C. S.; Eaborn, C.; Lappert, M. F. *J. Organomet. Chem.* **1972**, *44*, 291.

(16) Bovey, F. A. *High Resolution NMR of Macromolecules*; Academic: New York, 1972.

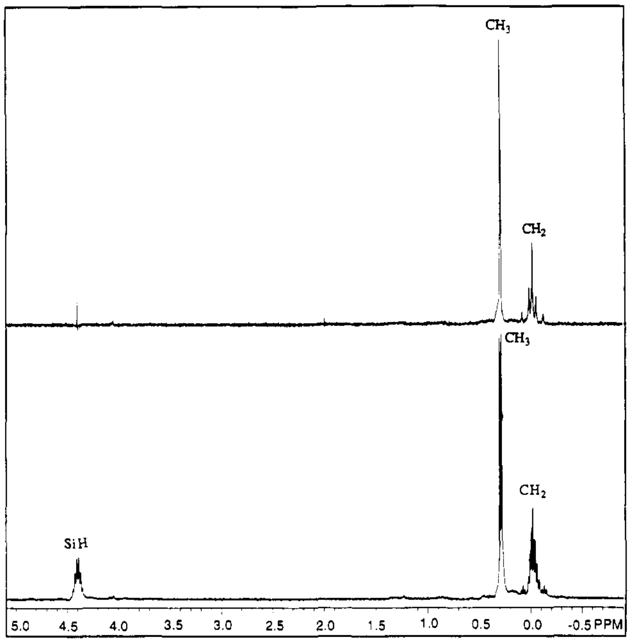

Figure 3. ^1H NMR spectrum of poly(silapropylene) and ^1H NMR spectrum of poly(silapropylene) with decoupling.

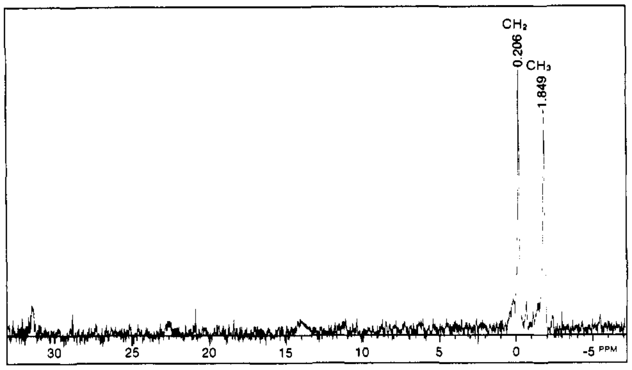

Figure 4. ^{13}C NMR spectrum of poly(silapropylene).

The reduction of poly[(chloromethylsilylene)methylene] by $LiAlH_4$ was carried out in ethyl ether. After the reduction, dilute acid was used to separate the salts. It has been suggested that this procedure may hydrolyze some Si–H bonds to give silanols or siloxanes.[4] However no hydrolysis was observed as a result of the aqueous workup that we carried out, as in indicated by IR (Table II) and ^1H, ^{13}C, and ^{29}Si NMR spectra. The effect of the differing configurations of the polymer can be seen clearly in the ^1H NMR spectra (Figure 3). The complicated splitting of the methylene protons is due to the coupling with Si–H and these configurational effects. The quintet observed for the methylene protons in the decoupled ^1H NMR spectrum is the result of configurational effects alone.

The reduction of the Si–Cl bond by $LiAlH_4$ has been observed to proceed with configuration inversion at the silicon atom.[17] No new steric centers should be produced during this reduction step. With the assumption that this ring-opening polymerization is not stereospecific or stereoselective, we expect that the probability for the occurrence of isotactic and syndiotactic sequences is equivalent. Inspecting the quintet of methylene protons in Figure 3, we find that the integration of the central peak resulting from the syndiotactic sequence and that of the remaining four peaks resulting from the isotactic sequence are the same. This observation confirms the equal mixing of syndiotactic and isotactic sequences. The ^{13}C (Figure 4) and ^{29}Si NMR spectra show only singlets, which may be due to the lesser influence of the Si–H bond on the configurational effect compared to the Si–Cl bond in poly[(methylchlorosilylene)methylene]. Also no terminal or branched groups are observed in these spectra. All the spectra show that the polymers we obtained have the same structures as that prepared by Bacque et al. except that no terminal groups were observed in our spectra, indicating that the polymers we prepared have much higher molecular weight.

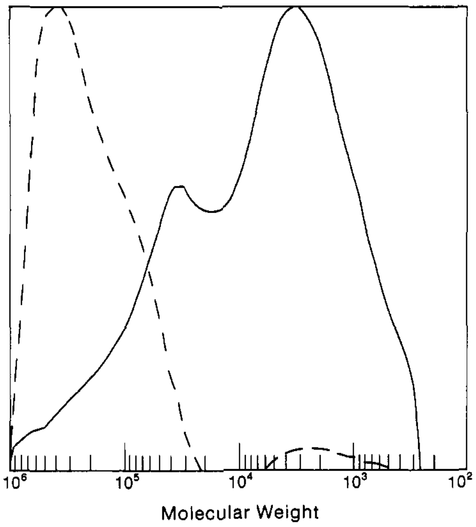

Figure 5. Molecular weight distribution of poly(silapropylene) (IV) [—] and poly(silapropylene) (IVa) [---] prepared with reduced amount of catalyst.

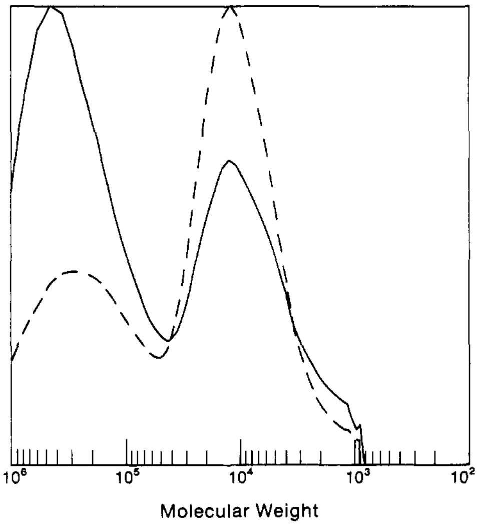

Figure 6. Molecular weight distribution of poly[(dimethylsilylene)methylene] carried out with 0.1% catalyst in hexane [---] and molecular weight distribution of poly[(dimethylsilylene)methylene] carried out with 0.4% catalyst in hexane [—].

The molecular weight distribution obtained from GPC for poly(silapropylene) (IV, 0.016 g of catalyst used) is shown in Figure 5. The number-average molecular weight (M_n) for this polymer was 6000, whereas the weight-average molecular weight (M_w) was 40 000. A similar bimodal distribution was also observed in the ring-opening polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (V) carried out in hexane and benzene. In the ring-opening polymerization of the neat liquid V, after the catalyst was mixed with the monomer and warmed by an 80 °C oil bath for several minutes, a rapid polymerization was observed, yielding an extremely viscous polymer. The polymer ob-

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[17] Corriu, R. J. P.; Cuerin, C. *Adv. Organomet. Chem.* **1982**, *20*, 265.

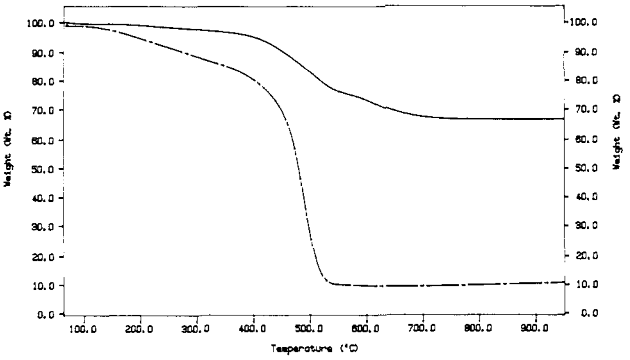

Figure 7. TGA plot of polysilapropylene (IV) [---] and TGA plot of poly(silapropylene) (IVa) after 400 °C heat treatment [—].

tained has a monomodal molecular weight distribution with M_n = 260 000 and a polydispersion index of 1.45. However in the polymerizations of V carried out in hexane or benzene, a gradual increase in the viscosity was observed during the whole refluxing period. A bimodal molecular weight distribution was invariably observed regardless of the amount of catalyst used, as is shown in Figure 6. However, both M_n and M_w seem to be dependent on the amount of catalyst employed (vide infra). The bimodal molecular weight distributions observed for polymerizations of II and V carried out in an inert solvent indicate that at least two mechanisms are functioning in the propagation of the polymers under these conditions.

In a second attempt at the ring-opening polymerization of II, a reduced amount of catalyst was employed (from 0.016 to 0.008 g). After reduction with $LiAlH_4$, a higher molecular weight polymer (M_n = 35 000, M_w = 292 750) with the same structure was obtained. The molecular weight distribution is shown in Figure 5. It is therefore apparent that the molecular weight of the polymer obtained can be increased by reduction in the amount of catalyst employed. This suggests a direct relationship between the amount of the catalyst used and the number of propagation centers in the polymerization. It is interesting that just the reverse effect was observed in the case of the polymerization of V in solution. As is clear from Figure 6, the higher amount of catalyst resulted in a shift of the molecular weight distribution to higher molecular weight. Additional experiments carried out using different solvents and different amounts of catalyst confirmed the general increase in molecular weight with catalyst concentration increase for compound V.

Thermolysis of Poly(silapropylene). The results of a TGA study of the pyrolysis of poly(silapropylene) (IV) under nitrogen is shown in Figure 7. The thermal stability up to 400 °C followed by a rapid decomposition between 400 and 500 °C is reminiscent of the behavior observed for the poly[(dimethylsilylene)methylene]. The yield (10%) is higher than that reported (5%)[4] for the poly(silapropylene) prepared by Bacque et al. The difference in the ceramic yield between these two polymers, which appear to have the same structure, may be due to the much higher molecular weight of the polymer that we have obtained. Consistent with this conclusion, it was found that the TGA of the even higher molecular weight poly(silapropylene) (IVa) obtained by using a smaller amount of catalyst was quite similar except that the ceramic yield in this case was 20%.

To improve the ceramic yield further, a change in the pyrolysis procedure is required. In contrast to the procedure employed by Yajima et al., which involves heat treatment in air to promote an oxidative cross-linking,[1] in this case a heating at 400 °C under nitrogen was effective in promoting cross-linking, therefore avoiding the contamination of the ceramic product by oxygen. A hard rubbery polymer was obtained after the 400 °C heating, which gave a 66% ceramic yield when heated to 1200 °C under nitrogen (Figure 7). The black pyrolysis product was further heated at 1600 °C for 4 h, yielding a broad X-ray diffraction pattern indicative of β-SiC.

This observation suggests that this high molecular weight linear polycarbosilane may have utility as a thermosetting precursor to SiC. An investigation of the cross-linking process induced by heating at 400 °C by the analysis of the gases evolved and spectroscopic measurements on the resultant polymeric product is currently in progress as well as studies of the chemical functionalization of the intermediate chloro polymer. The results of these investigations along with those directed at the study of the pyrolytic conversion of the polymer to a ceramic material will be reported subsequently.

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