

Figure 16. Constant current discharges of a Li/TiS₂ cell using 87 MEEP/13 PVP-(LiClO₄)_{0.25} electrolyte at C/20 and different temperatures. $i_d = 0.08 \text{ mA/cm}^2$; $i_c = 0.04 \text{ mA/cm}^2$; voltage limits = 1.6–3.0 V.

overcharge, did not have a deleterious effect on subsequent cell performance.

The performance of a Li/TiS₂ cell using a mixed polymer electrolyte is illustrated with the MEEP-PVP-(LiClO₄)_{0.25} electrolyte, at three different temperatures and 0.05 mA/cm² (C/20) (Figure 16). At room temperature the cell delivered about 17% (0.14 mAh/cm²) of its theoretical cathode capacity of 0.88 mAh/cm². At 75 °C, the cathode utilization was 100%. The charging efficiency at room temperature was 85%, and at the higher temperature it was 100%, indicating slower recharge kinetics at low temperatures. The rate capability of the cell containing MEEP/PVP-(LiClO₄)_{0.25} was very much similar to that of the cell described above utilizing MEEP-(LiClO₄)_{0.25}.

Cells utilizing MEEP/PEO-(LiClO₄)_{0.13} composite electrolytes exhibited rate capabilities inferior to those described above. For example, a Li/TiS₂ cell utilizing 70 wt % MEEP:30 wt % PEO-(LiClO₄)_{0.12} could not be discharged at room temperature at a practical rate such as C/20 or C/40. However, when it was discharged at 65 °C, about 86% of the theoretical cathode capacity, i.e., 1.2

mAh/cm² was obtained at the C/40 rate, while at 50 °C the utilization was 0.96 mAh/cm². The Coulombic efficiency during cycling was close to 100%.

Conclusions

Several relatively simple methods have been developed to prepare dimensionally stable MEEP-based electrolytes. Pure MEEP when complexed with LiAlCl₄ forms dimensionally stable, free-standing thin films. This contrasts the behavior of MEEP complexes we have prepared with many other commonly used Li salts. Additional methods of dimensional stabilization include blending MEEP-(LiX)_n with a poly(olefin oxide) such as PEO or PPO, or forming composites with photopolymers such as PEGDA and PVP. Some of these electrolytes exhibited conductivities close to those of the dimensionally unstable MEEP-(LiX)_n, indicating that they retain a high degree of plasticity or domains of microfluidity. Transport numbers ranging between 0.4 and 0.5 have been determined for Li⁺ in these electrolytes, which are very similar to that obtained in other Li⁺-conductive polymer electrolytes. The dimensionally stabilized MEEP-based electrolytes have demonstrated good electrochemical stability on a number of metal substrates including Li. The long-term cycling capability of Li/TiS₂ secondary solid-state cells fabricated with these electrolytes indicate that they are useful for low-to-moderate rate applications at ambient temperature.

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Registry No. PEO, 25322-68-3; PPO, 25322-69-4; PVP, 9003-39-8; PEGDA, 28158-16-9; LiBF₄, 14283-07-9; LiClO₄, 7791-03-9; LiAsF₆, 29935-35-1; LiCF₃SO₃, 33454-82-9; LiAlCl₄, 14024-11-4; LiN(SO₂CF₃)₂, 90076-65-6.

New Poly(carbosilane) Models. 4. Derivatization of Linear Poly[(methylchlorosilylene)methylene]: Application to the Synthesis of Functional Poly(carbosilanes) Possessing a Poly[(methylsilylene)methylene] Backbone

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To study the mechanisms of pyrolysis of poly(carbosilanes), as well as the effect of the structure of these precursors upon properties of the resulting ceramics, novel organosilicon polymers with well-defined skeletons were prepared. Thus, linear poly(carbosilanes) formed of exactly alternate silicon atoms and methylene groups were synthesized. Owing to the presence of functional groups on silicon centers, cross-linking of these compounds was then investigated according to chemical routes, by creating disilane, disilazane, disiloxane, and hydrocarbon bridges between different poly(carbosilanic) sites. These polymers were characterized by physicochemical methods (IR, NMR, GPC, and TGA).

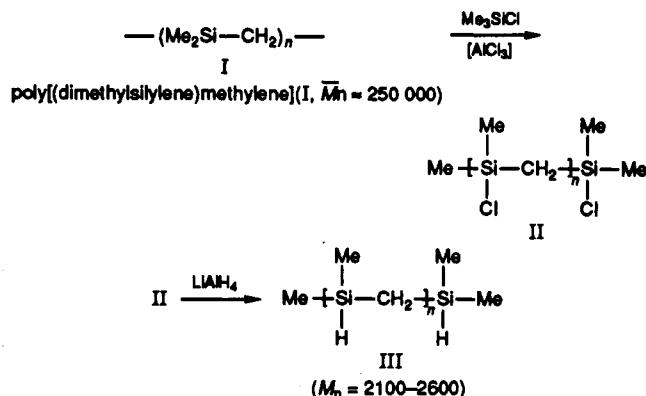
Introduction

The need for ceramic composites offering enhanced properties requires both continual improvement of previously reported processes and elaboration of new synthetic routes to these materials. Thus, industrial-scale production

of SiC fibers by pyrolysis of poly(carbosilanes) (PCS), according to Yajima's route, demonstrates the considerable interest in organometallic precursors.¹

(1) Yajima, S. *Ceram. Bull.* 1983, 62, 993.

Scheme I. Synthesis of Linear Poly[(methylchlorosilylene)methylene] (II) and Poly(silapropylene) (III)



However, this route has several inherent drawbacks affecting the silicon carbide fibers as well as the starting poly(carbosilanes). For example, it still remains necessary to improve a number of ceramic fiber properties, such as oxidation resistance and thermomechanical behavior.² Moreover, although the starting PCS skeletons are known to contain mainly alternate silicon atoms and methylene groups (i.e., Si-substituted silylenemethylene unit¹), these compounds exhibit complex polymeric structures that have not yet been fully elucidated. Elemental poly(silapropylene) units, $-(\text{MeHSiCH}_2)_n-$, are probably present, as inferred from spectroscopic data, but they are part of a strongly branched framework.^{3,4}

On the other hand, very little is known about the mechanisms of the thermal conversion of PCS into silicon carbide. So, it remains difficult to find relationships between the structure of organometallic precursors and preceramic polymers and both the microstructure and properties of the obtained ceramics.

To improve our understanding of the thermal conversion of PCS into silicon carbide, it was necessary to establish suitable models. In a previous paper, we reported the conversion of linear poly[(dimethylsilylene)methylene], I, into a poly[(methylchlorosilylene)methylene], II, and subsequent reduction of this last polymer affording poly(silapropylene), III (Scheme I). We have shown that this novel poly(carbosilane) can be regarded as a convenient linear model of Yajima's PCS.^{5,6}

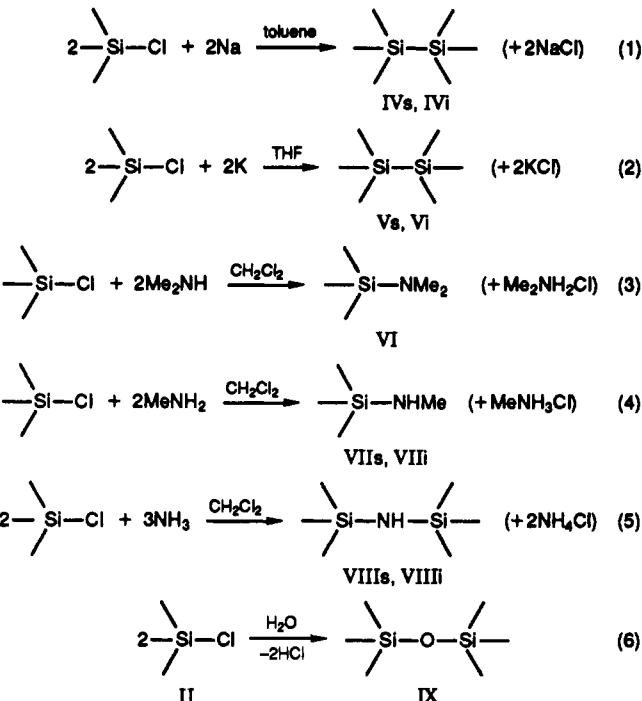
More recently, Interrante et al. reported the preparation of the same polymers but with higher molecular weights, using also a ring-opening polymerization route.²¹

Here, we report the preparation and characterization of a series of functional poly(carbosilanes) formed from poly[(methylsilylene)methylene] chains upon derivatization of II and III, as depicted in Schemes II and III.

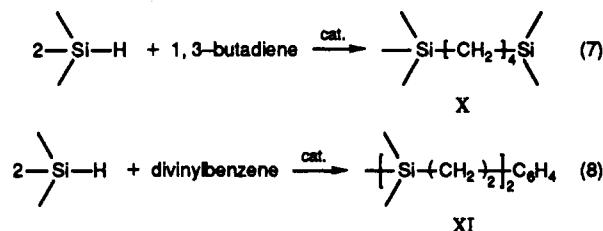
Experimental Section

General Procedures. Solvents: Toluene was dried over sodium by refluxing during several hours and then distilled under argon. THF was distilled under argon just before use from benzophenone–sodium until the appearance of a persistent blue

Scheme II. Reactions of Poly[(methylchlorosilylene)methylene] (II)



Scheme III. Hydrosilylation Reactions Using Poly(silapropylene) (III) in the Presence of Speier's Catalyst



color. Ether was first dried over calcium chloride and then distilled under argon from benzophenone–sodium. All of the solvents were stored over on molecular sieves.

Apparatus: All the reaction vessels were oven dried (90 °C) and purged with argon prior to use. All manipulations involving air-sensitive materials were carried out using an argon vacuum line or a glovebox.

Characterization: Molecular weights were determined by gel permeation chromatography (GPC) using five μ -Styragel columns (porosity ranges of 100, 500, 10³, 10⁴, and 10⁵ Å) and THF as the eluent at a flow rate of 1 mL/min. Molecular weights were obtained from polystyrene standards. The detection system was a Waters Associates R 401 differential refractometer.

Proton NMR spectra were obtained on a Hitachi Perkin-Elmer R 24B spectrometer (60 MHz) or a Bruker AC 200 spectrometer, with polymer solutions in CDCl_3 or C_6D_6 and TMS as the external standard.

Infrared spectra were determined on a Perkin-Elmer 1420 spectrometer (in the region 4000–600 cm^{-1}) or a Perkin-Elmer 983 spectrometer (in the region 4000–200 cm^{-1}) with product films respectively between NaCl and Tl(BrI) plates.

Thermogravimetric analyses were performed on a Perkin-Elmer TGS 2 analyzer (3600 data station, heating rate 5 °C/min; argon flow rate 40 mL/min).

Elemental analysis of polymers was carried out by the Service Central d'Analyse du CNRS, B.P. 22, F-69390 Vernaison. Residual chlorine and oxygen ratios were also measured in a few cases, even if these elements theoretically were not present.

Syntheses. Preparation of I: Poly[(dimethylsilylene)methylene], I, was prepared in quantitative yield by ring-opening polymerization of 1,1,3,3-tetramethyldisila-1,3-cyclobutane ac-

(2) Simon, G.; Bunsell, A. *J. Mater. Sci. Lett.* 1983, 2, 80.

(3) Yajima, S. *Advanced Fibers and Composites for Elevated Temperature*; Ahmad, I., Noton, B. R. Eds.; Conferences Proceedings, 1979; p 29.

(4) Hasegawa, Y.; Okamura, K. *J. Mater. Sci.* 1986, 21, 321.

(5) Bacqué, E.; Pillot, J.-P.; Birot, M.; Dunoguès, J. *Macromolecules* 1988, 21, 30.

(6) Bacqué, E.; Pillot, J.-P.; Birot, M.; Dunoguès, J. *Macromolecules* 1988, 21, 34.

cording to the previously reported procedure.⁷

Preparation of II: Polymer I (75 g) and trimethylchlorosilane (510 g, large excess) were introduced into a two-neck 500-mL flask equipped with a spinning band column and an argon inlet. This mixture was magnetically stirred at room temperature to dissolve a large amount of polymer I. Anhydrous aluminum trichloride (5.8 g) was then added, and the viscous brown mixture was heated to reflux for several hours until the first drops of tetramethylsilane began to condense at the top of the column, resulting in a marked decrease of the reflux temperature from the range 55–57 °C (i.e., Me_3SiCl boiling point) to 22–28 °C. Sometimes, addition of a few grams of catalyst is necessary to start the reaction. At this time, a significant fluidization of the mixture occurred, and the TMS was slowly distilled as soon as the reaction proceeded. After several hours, the rate of its formation decreased. When the TMS distillation was completed, the mixture was allowed to cool to room temperature under argon. After filtration under inert atmosphere to remove any solid material, the excess of trimethylchlorosilane was distilled off by using a rotary evaporator, and the crude product carefully devolatilized under high vacuum, affording a dark brown viscous polymer (90.5 g, 94% yield). The \bar{M}_n of II was found to vary in the range 2100–2600 according to different runs.

Preparation of III: LiAlH_4 (9.1 g, 0.239 mol) and ether (200 mL) were placed into a 500-mL three-necked flask equipped with a dropping funnel, a thermometer well, and a condenser. The flask was placed in an ice bath, and polymer II (29.4 g) in solution in ether (150 mL) was then added dropwise with magnetic stirring. At the end of the addition, the mixture was refluxed for 24 h and left at room temperature without stirring to allow precipitation of the solid aluminum salts. The liquid portion was then transferred into another flask, and the ether stripped off under high vacuum. The remaining grey solid was washed twice with hexane (100 mL), and dilute HCl (a few milliliters of 4 N solution) was then slowly added at 0 °C with stirring to the combined liquid fractions (under argon). The organic layer was decanted, washed three times with cold distilled water, and dried (Na_2SO_4), and the solvent removed under high vacuum (10^{-1} Torr) to yield a pale yellow mobile oil (17.5 g, 95% yield). The IR spectrum of this product did not exhibit any shoulders nor broadening of the intense absorption at 1040 cm^{-1} [$\omega(\text{Si}-\text{CH}_2-\text{Si})$ band]. Thus it can be inferred that completion of the reduction has occurred and therefore that no appreciable amount of Si–H or remaining Si–Cl bonds have been hydrolyzed.

Preparation of IVs and IVi: The apparatus consisted of a 100-mL, three-neck flask equipped with a magnetic bar, fitted with a dropping funnel, a thermometer well, and a condenser cooled by Decalin at –10 °C, connected to a CaCl_2 column. Xylene (10 mL) and sodium (3.45 g, 50% molar excess) were successively introduced under an argon stream and heated to reflux with vigorous stirring. A solution of poly[(methylchlorosilylene)-methylene], II (9.26 g, approximately 0.1 mol (1 mol corresponds to 92.5 g of $(\text{MeClSiCH}_2)_n$), residual oxygen <3.5%), in xylene (40 mL) was then added over 10 min to a suspension of molten sodium, and the reaction mixture was kept at reflux for 5 days. After cooling, the mixture was centrifuged to separate solid and liquid phases. The solid was washed with xylene and centrifuged twice, and the combined solutions were concentrated by using a rotary evaporator. Devolatilization under reduced pressure led to a yellow viscous polymer, IVs (2.25 g, 39.4% yield). The solid fraction was successively triturated by methanol (100 mL) and water (100 mL), and then filtered off. The residual solid was then washed twice with acetone and ether and dried under vacuum. The weight of this insoluble and unmeltable fraction, IVi, was of 4.5 g. The overall weight of this polymer was found to be appreciably greater than the expected value, likely due to the presence of oxygen incorporated with the product upon hydrolysis of residual silicon–chlorine bonds. This assumption was supported by the IR spectrum of IVi fraction, showing a medium-intensity band at 1050 cm^{-1} [$\nu(\text{Si}-\text{O}-\text{Si})$].

Preparation of Vs and Vi: With use of a similar apparatus, a solution of polymer II (16.0 g, ≈ 0.173 mol) in 70 mL of THF was poured slowly onto a suspension of molten potassium (6.8

g, 0.174 mol) in refluxing THF (100 mL) over 50 min. After refluxing for 75 h, the mixture was allowed to cool to room temperature. A similar workup as for IVs afforded Vs as a soluble but unmeltable solid (4.82 g, 49% yield) and an unmeltable insoluble solid Vi (7.3 g).

Preparation of VI: A 500-mL three-necked flask was fitted with a reflux condenser cooled by ethanol at –30 °C and connected to a potassium hydroxide column, a thermometer well, and a dropping funnel. After careful purging with dry argon, dichloromethane (50 mL) and dimethylamine (9.75 g, 0.221 mol) were introduced (using a syringe for the amine) and cooled at –40 °C in a dry ice–acetone bath. A solution of II (9.5 g, 0.103 mol) in dichloromethane (100 mL) was then added over 75 min with vigorous stirring. This mixture was allowed to warm again and kept at room temperature for 20 h, and the solvent removed under high vacuum. The crude product was treated with pentane and filtered off to separate any residual amine hydrochloride, and this workup repeated several times. After careful devolatilization, a viscous orange oil was recovered and stored under argon at –20 °C (9.8 g, 94.4% yield); residual chlorine percentage 0.7%.

Preparation of VII: An apparatus similar to that used for dimethylamine was used, but the dropping funnel was replaced by a gas inlet with a sparge attachment for bubbling monomethylamine inside the vessel. After careful purging of the system with argon, a solution of polycarbosilane II (9.5 g, 0.103 mol) in dichloromethane (200 mL) was placed into the vessel under argon and cooled to 0 °C. The gaseous monomethylamine was bubbled in at 0 °C with vigorous stirring; the internal temperature gradually raised to 12 °C before decreasing slowly. After 1 h, the pale yellow mixture containing condensed monomethylamine was allowed to warm to room temperature, whereupon the excess amine evaporated slowly under low vacuum. The amine hydrochloride precipitate was separated by filtration and washed twice with dichloromethane. The combined organic solutions were concentrated with a rotary evaporator, and traces of solvent removed overnight under high vacuum, affording a yellow solid, VII_a, which was kept at –20 °C (8.1 g, 90.6% yield).

A similar experiment was performed without solvent, starting from 13.7 g of II. The usual workup led to a yellow viscous soluble liquid, VII_b, with only 48.5% yield, (6.25 g).

Preparation of VIII: Into a similar vessel, a solution of polymer II (16.6 g, 0.179 mol) in dichloromethane (250 mL) was introduced, and ammonia gas bubbled through the solution at 0 °C with vigorous stirring. The initially brown solution readily turned white, whereas the maximum internal temperature increased to 41 °C before decreasing to 20 °C. After 1 h more at this temperature, the mixture was refluxed during 3 h and allowed to cool at room temperature. Centrifugation allowed separation of a white solid and an orange liquid. The solid fraction was washed twice with dichloromethane and filtered off. The solutions were then combined and filtered again. The filtrate was concentrated with a rotary evaporator and devolatilized overnight under high vacuum, affording a yellow solid, VIII (8.95 g, melting interval 90–100 °C). On the basis of the theoretical linear formula, the yield was of 77.5% (expected weight 11.54 g). The elemental analysis gave a very low residual chlorine ratio (0.6%). Within a few days, VIII was found to give an insoluble and unmeltable polymer when kept at room temperature. Therefore it must be stored under inert gas at –20 °C. The insoluble part was treated with water, yielding a grey solid (6.1 g), which was not further characterized.

Preparation of IX: A solution of polycarbosilane II (5.05 g, 0.054 mol) in THF (25 mL) was slowly poured onto a mixture of water (10 g) and THF (10 mL), with vigorous stirring. After refluxing overnight, the solvent and water were removed under high vacuum during several hours, affording a brown solid (3.48 g, 98% yield); softening range 120–140 °C.

Preparation of X and XI: 1,3-Butadiene (1.4 g, 0.026 mol) was condensed into a 500-mL glass tube carefully purged with argon. Polymer III (3 g, 0.051 mol) and a few milligrams of catalyst ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) were then introduced. The glass tube was then frozen in liquid nitrogen and sealed under vacuum. This vessel was placed into an autoclave and heated at 200 °C during 24 h. After cooling, the sealed tube was opened and the excess butadiene removed under high vacuum at 200 °C, yielding an insoluble, unmeltable yellow solid X 4.2 g, 96.8% yield, expected 4.39 g.

Table I. Elemental Analysis of Poly(carbosilane) Models

model polym	C	H	N	Si	Cl	O
I	50.11 (49.96)	11.47 (11.10)		38.10 (38.94)		
II	26.65 (26.28)	5.60 (5.58)		30.20 (30.13)	37.20 (38.03)	3.00
III	41.60 (41.67)	10.35 (10.66)		<i>a</i> (47.77)		2.75
IVs	40.55 (42.10)	7.81 (8.78)		<i>a</i> (49.12)	4.20 ^b	
Vs	45.51 (42.10)	7.84 (8.78)		(49.12)	3.80 ^b	4.20
VI	46.40 (47.48)	10.53 (10.96)	12.50 (13.84)	29.20 (27.75)	0.70 ^b	
VII _a (branched)	43.27 (41.96)	9.41 (9.09)	10.21 (9.79)	(39.16)	0.20 ^b	
VIII _a (branched)	35.78 (37.20)	8.29 (8.52)	7.57 (10.85)	(43.41)	0.50 ^b	
IX	35.97 (36.92)	7.23 (7.69)		(43.08)	1.5 ^b	12.93 (12.31)

^a Unreliable analysis; see also ref 12. ^b Remaining Cl percentage.

A similar experiment was carried out with III (2.9 g, 0.05 mol) and divinylbenzene (3.3 g, 0.253 mol), yielding an insoluble and unmeltable polymer XI (5.92 g, 96% yield).

Results and Discussions

Dechlorination of Poly(carbosilane) II by Alkali Metals. To obtain favorable yields of SiC, the need for preceramic polymers with highly branched structures has been previously recognized.^{8,9} On the other hand, linear polycarbosilanes such as poly[(dimethylsilylene)methylene], I, and poly(silapropylene), III, gave only poor char yields.^{6,10} Owing to the presence of chemically reactive Si—Cl bonds, polymer II was therefore expected to enable us to obtain access to a series of novel cross-linked poly(carbosilanes).

First, we investigated the coupling of this polymer by using alkali metals: sodium in xylene and potassium in THF. Indeed, dechlorination of chlorosilanes by alkali metals was known to afford disilane bonds,¹¹ and it was therefore interesting to investigate the thermal behavior of new polycarbosilanes processing well-defined backbones comprised of Si—CH₂ units and Si—Si chemical bridges, i.e., polymer(silacarbosilanes) (Scheme II, eqs 1 and 2). It is likely that these two kinds of units are present in the Japanese PCS Mark III, whereas PCS Mark I contains mainly Si—CH₂ linkages.¹

Preparation of Polymers IVs and IVi. The reaction of polymer II with molten sodium in boiling xylene gives a meltable polymer, IVs, accompanied by an insoluble and unmeltable fraction, IVi, in respective ratios close to 1:2. IVs was fairly soluble in common organic solvents such as THF, hydrocarbons, and aromatic solvents. GPC curves of IVs and II displayed maxima located at the same positions, whereas a small high-mass hump, in the case of IVs, was assigned to more cross-linked products undergoing a strong increase in the average mass molecular weights (Figure 1).

The elemental analysis of IVs revealed the presence of an appreciable amount of remaining chlorine (Table I), showing that complete consumption of the silicon—chlorine bonds is somewhat difficult under these conditions, whatever the reaction time. Analysis of silicon was found unreliable in the case of IVs (as well as several other compounds of this series). Indeed, the difficulty to obtain values for carbon and silicon in good agreement with those expected has already been point out by other authors in the case of preceramic polymers.¹²

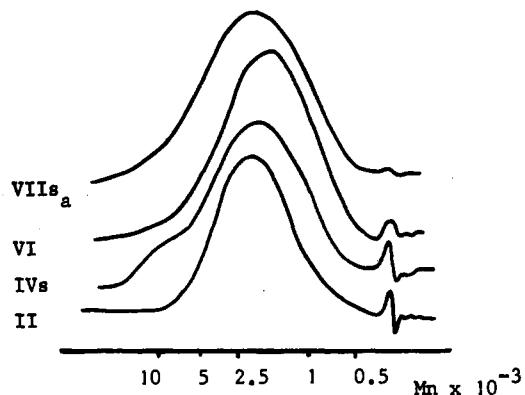


Figure 1. GPC curves of poly[(methylchlorosilylene)methylene] (II), poly(silacarbosilane) IVs, and poly(carbosilazanes) VI and VII_a.

Table II. GPC and TGA Data for Model Poly(carbosilanes)

compd	av no. mol wt \bar{M}_n	polydispersity	ceram yield (950 °C), %
I	250000	1.5	3.5
II	2300–2600	2.0–2.5	
III	2100	1.9	5
IVs	4250	5.7	11.4
IVi	<i>a</i>	<i>a</i>	77.6
Vs	4930	6.1	43.5
Vi	<i>a</i>	<i>a</i>	59.3
VI	2480	1.7	33.5
VII _a	3580	3.1	24.7
VII _b	3940	4.0	53.0
VIII _a	4120	8.9	37.5
IX	2960	2.5	54.3
X	<i>a</i>	<i>a</i>	14
XI	<i>a</i>	<i>a</i>	24.7

^a Polymer insoluble in THF or toluene.

Because both intra- and intermolecular condensations can be expected, we can reasonably assume that the IVs fraction consists primarily of polymers resulting mainly from intramolecular reactions, i.e., without appreciable chain length change but with creation of small rings (intermolecular pathways likely occur only to a small extent) as inferred from \bar{M}_n values (Table II). On the other hand, IVi appeared to be more cross-linked as a consequence of more intermolecular condensations, which role led to a strong increase in molecular weights resulting in the obtention of an insoluble and unmeltable polymer (Scheme IV).

Upon careful devolatilization, the overall weight of poly(silacarbosilane) that was recovered slightly exceeded the expected value. This observation suggests that the solvent is incorporated within the product to a small extent. This assumption is supported by spectroscopic data as the ¹H NMR spectrum of IVs exhibited two broad signals centered at 0.6 and 0.15 ppm, respectively assigned

(8) Schilling, C. L., Jr.; Wesson, J. P.; Williams, T. *Ceram. Bull.* 1983, 62, 912.

(9) Wynne, K.; Rice, R. *Annu. Rev. Mater. Sci.* 1984, 14, 297.

(10) Levin, G.; Carmichael, J. B. *J. Polym. Sci.* 1968, 6(A-1), 1.

(11) Eaborn, C. *Organosilicon Compounds*; Butterworths Scientific: London, 1980.

(12) Schilling, C. L., Jr. ONR Technical Report, No. AD-A141546, 1983.

Scheme IV. Cross-Linked Structures Resulting from Dechlorination of II in the Presence of Sodium or Potassium

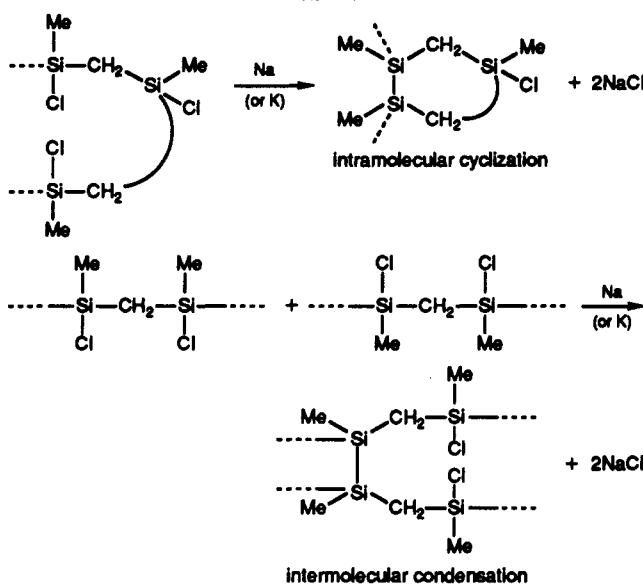


Table III. ^1H and ^{29}Si Chemical Shifts for Model Poly(carbosilanes)

polym	$\delta(^1\text{H})$	$\delta(^{29}\text{Si})$
II	0.63 (CH_3), ^a 0.53 (CH_2) ^b 0.75 (CH_2), ^a 0.66 (CH_2) ^b	25.5 ^a 28.4 ^b
III	0.25 (CH_3), ^a 0.13 (CH_3) ^b -0.06 (CH_2), ^a -0.22 (CH_2) ^b 4.34 (H_{Si}), ^a 4.05 (H_{Si}) ^b	-15.5 ^a -15.9 ^b
IVs, Vs	0.60 (CH_3), ^c 0.30-0.0 (CH_3 , CH_2) 2.39 [$\text{N}(\text{CH}_3)_2$], 0.10 (CH_3) -0.18 (CH_2)	-19.0, 21.5 ^c 4.95
VIIIs _a	0.15 (CH_3), 0.07 (CH_3), -0.16 (CH_2) 2.50, 2.41 (NCH_3)	4.5
VIIIIs	0.15 (CH_3 , HN), -0.13 (CH_2)	0.0
IX	0.10 (CH_3), 0.0 (CH_2)	2.2

^a Internal nuclei. ^b Terminal nuclei. ^c Signals due to remaining Si-Cl bonds.

to remaining CH_3SiCl and $\text{CH}_3\text{Si}-\text{Si}$ plus $\text{CH}_2\text{Si}-\text{Si}$ protons (Table III). Small amounts of aromatic and benzylic protons were also detected. The ^{29}Si NMR spectrum is in good agreement with a partial condensation as two broad signals at about -19 (Si-Si) and 21.5 ppm (remaining Si(-Cl) nuclei) are present. The IR spectrum of this product (Figure 2) corroborates this as we observe a strong absorption at 477 cm^{-1} and a shoulder at 440 cm^{-1} , respectively assigned to $\nu(\text{Si}-\text{Cl})$ and $\nu(\text{Si}-\text{Si})$ vibrations, whereas a weak band at 2100 cm^{-1} [$\nu(\text{Si}-\text{H})$] revealed that reduction of Si-Cl groups also occurred as a side reaction.

The IR spectrum of IVi exhibited a strong $\nu(\text{Si}-\text{H})$ band and a weak $\nu(\text{Si}-\text{Si})$ band respectively at 2100 and 441 cm^{-1} , whereas the $\nu(\text{Si}-\text{Cl})$ absorption could not be detected in this spectrum.

Synthesis of Polymers Vi and Vs. Dechlorination of polymer II using potassium in THF afforded an orange soluble, unmeltable solid, Vs, and an insoluble, unmeltable solid, Vi (Vi/Vs ratio = 1.5). Vs exhibited weak solubility in the usual organic solvents despite the fact that it initially was soluble in THF. IR spectra of Vs and Vi exhibited the characteristic absorptions of Si-H (2100 cm^{-1}) and Si-Si (430 cm^{-1}), whereas Si-O-Si, Si-O-C (broad absorption between 1050 and 1200 cm^{-1}), and alkane units (1450 cm^{-1}) also were observed (Figure 2). Incorporation of THF probably was responsible for the presence of oxygen as well as for the alkane bands. This side reaction

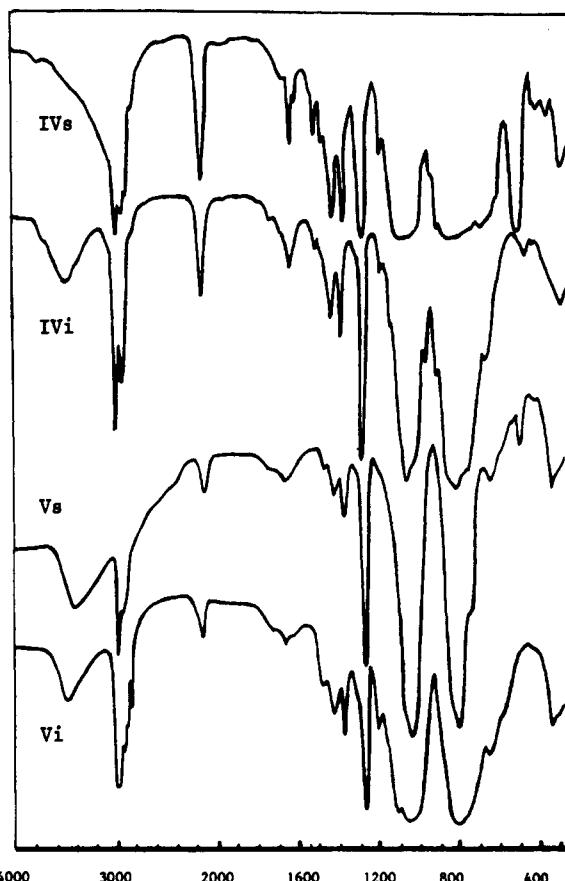


Figure 2. IR spectra of poly(carbosilanes) obtained upon treatment of II respectively in the presence of sodium (IVs, IVi) and potassium (Vs, Vi).

accounts for the fact that the overall weight of the product exceeded the expected value. Finally, a weak band corresponding to the remaining Si-Cl bonds (474 cm^{-1}) was observed only in the case of Vs. This was corroborated by elemental analysis, which revealed the presence of residual chlorine ($\approx 3.8\%$), as in the case of IVs. Therefore potassium in THF seemed more efficient than sodium in xylene for cross-linking the chlorinated PCS II, as only unmeltable products (i.e., more cross-linked polymers) were obtained. However side reactions occurred in such a way that the structure and the composition of the products were more complex than initially expected.

From the above results, it can be inferred that intramolecular and intermolecular condensations occurred simultaneously upon treatment of II by sodium or potassium, resulting in the formation of cyclic structures. The former process accounts for the fact that the main hump of the IVs GPC profile was similar to the mass distribution curve of the starting material but with a slightly decreased \bar{M}_n value. In the second case, condensation of at least two molecules via creation of a silicon-silicon bond between two different chains afforded insoluble and unmeltable high molecular weight products exhibiting a significant increase in the average molecular weights and polydispersity. So, the resulting poly(silacarbosilane) can be regarded as a complex framework of cyclic structures having different sizes. There is also good evidence for incorporation of the solvent with the products. Similar phenomena were previously mentioned in the case of condensations using Na/K alloy,¹² whereas the formation of Si-H bonds suggested that silicon-centered radicals or anions were involved during the dechlorination by alkali metals, as previously inferred by Zeigler.¹³ The poor ability of such

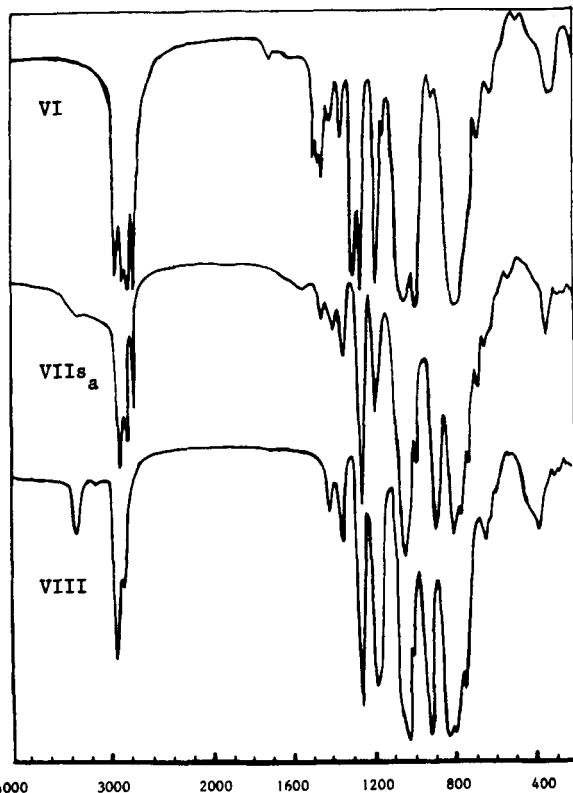


Figure 3. IR spectra of poly(carbosilazanes) obtained upon treatment of II respectively by dimethylamine (VI), mono-methylamine (VIIIs_a), and ammonia (VIIIs).

radicals to homocouple might result from steric hindrance combined with poor mobility when the rigidity of structures increase, resulting in competitive hydrogen abstraction from the solvent. It is obvious that, in such rigid structures, the greater the steric hindrance and insolubility, the more inaccessible the silicon–chlorine bonds will be.

Reaction of Poly(carbosilane) II with Amines: Synthesis of Novel Model Poly(carbosilazanes). We turned then to the synthesis of new poly(carbosilazanes) (PCSZ), i.e., organosilicon polymers containing C–Si–N linkages in the main backbone, by reacting the chlorinated polymer II with amines (Scheme II, eq 3–5). Ammonia and primary amines usually condense with chlorosilanes, leading to disilazanes and to the elimination of amine hydrochlorides.^{11,14,15}

Action of Dimethylamine: Preparation of VI. Dimethylamine and polymer II were reacted in dichloromethane, resulting in the precipitation of a white solid (dimethylamine hydrochloride) and an orange viscous polymer, VI, which flowed at room temperature (94% yield after careful devolatilization, residual chlorine ratio 0.7%). This product was found to be very sensitive to moisture.

Polymer VI and (dimethylamino)trimethylsilane, $\text{Me}_3\text{SiNMe}_2$, exhibit very similar IR spectra, except for the additional characteristic $\text{Si}-\text{CH}_2-\text{Si}$ absorption at 1040 cm^{-1} in the case of VI (Figure 3). The ^1H NMR spectrum of VI exhibits a broad singlet at 2.39 ppm for the NMe_2 protons and a singlet at 0.10 ppm for the MeSi protons. The $\text{Si}-\text{CH}_2-\text{Si}$ protons give an AB spectrum ($J_{\text{AB}} = 14.2$ Hz) and a broad singlet (A_2 spectrum) both centered at -0.18 ppm (Figure 4). The integration ratio is consistent with the expected linear structure. These patterns are

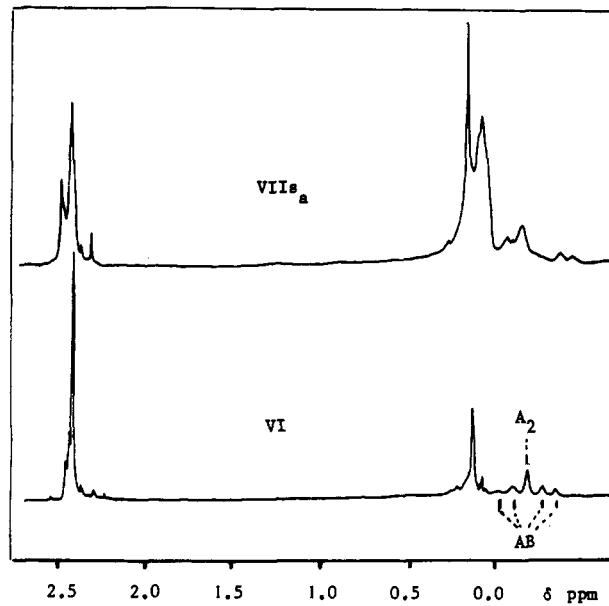


Figure 4. ^1H NMR spectra (200 MHz) of poly(carbosilazanes) VI and VIIIs_a.

similar to those previously observed in the case of II and III;⁶ they result from diad effects induced by the two adjacent asymmetric silicon atoms whereas their respective intensities correspond roughly to the statistical ratio, i.e., 0.66:0.33. This is consistent with the fact that VI is a random polymer, which is expected given that the starting chlorinated PCS II is also a random polymer.^{5,6}

The ^{29}Si NMR spectrum of VI exhibits a broad singlet at 4.95 ppm and a very small singlet at 5.95 ppm, respectively assigned to the internal and terminal silicon atoms ($\delta(^{29}\text{Si}) = 5.9$ ppm for the monomeric compound $\text{Me}_3\text{SiNMe}_2$ ¹⁶). As expected, the average number molecular weight of II and VI, as well as their polydispersity indexes, were similar (II: $\bar{M}_n \approx 2300\text{--}2600$, $\rho = 2.0\text{--}2.5$; VI: $\bar{M}_n \approx 2480$, $\rho = 1.7$).

Action of Monomethylamine: Preparation of VII. Poly[(methylchlorosilylene)methylene] was reacted with monomethylamine under similar conditions (Scheme II, eq 4). After separation of the amine hydrochloride and evaporation of the solvent, a yellow soluble solid polymer, VIIIs_a, was obtained (91% yield, melting interval 50–60 °C); residual chlorine ratio $\approx 0.2\%$. The IR spectrum of VIIIs_a was consistent with the expected structure. Its ^1H NMR spectrum was very similar to that of VI (Figure 4). For example, the methylene protons give broad upfield signals forming AB and A_2 patterns. On the other hand, the integration ratio reveals significant lowering of the intensity of the NMe signals, showing that $\text{Si}-\text{NMe}-\text{Si}$ bridges were formed to a large extent, instead of pendant NHMe groups. It is to be inferred that this novel cross-linked poly(carbosilazane) contains ring structures resulting from intramolecular or intermolecular condensations (Scheme V). This result is also supported by the nitrogen content, which was found close to the value expected for the branched structure (found 10.21%, calculated values respectively for the linear and the cross-linked structures 16.09% and 9.79%).

This pathway accounted for the fact that VIIIs_a is a solid and for the broadening of the signals observed in the ^1H NMR spectrum. Moreover, the GPC curve was in good agreement with these phenomena, as a considerable in-

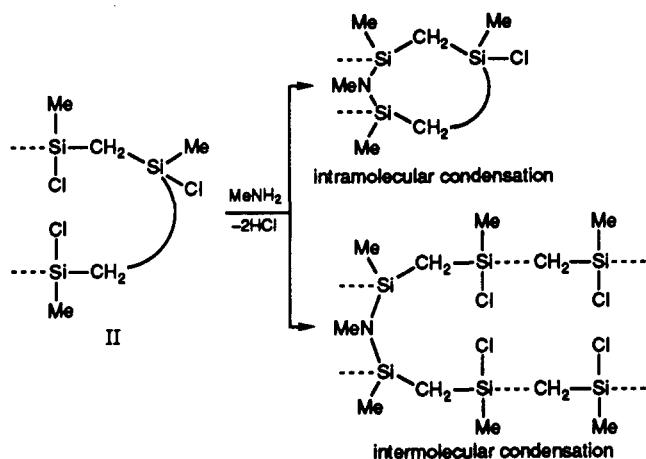
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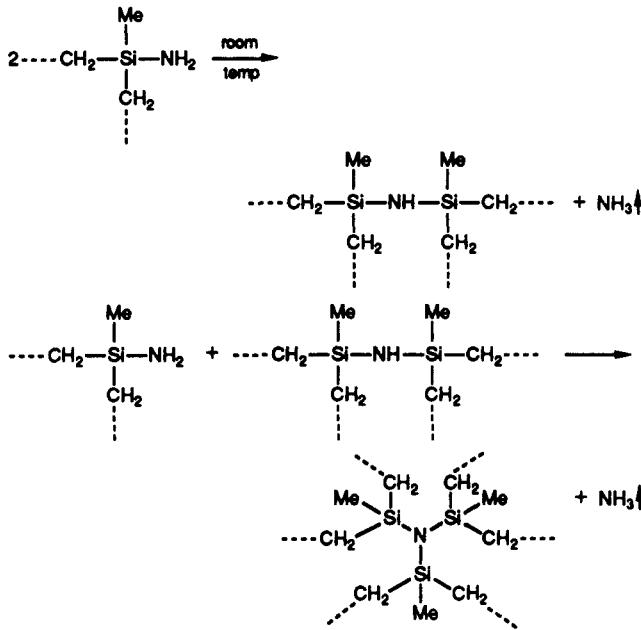
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Scheme V. Formation of Disilazane Bridges upon Reaction of Monomethylamine with II via Intramolecular and Intermolecular Condensations



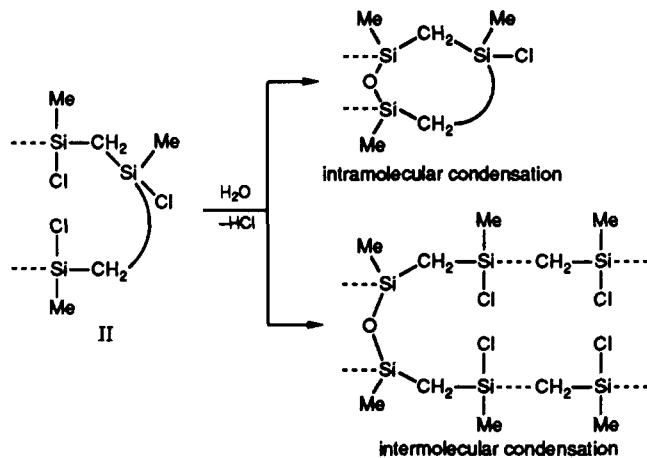
Scheme VI. Reticulation of Poly(carbosilazane) VIII via Transamination Pathways



crease in the average molecular weight was observed ($\bar{M}_n \approx 3580$). When the reaction was performed without solvent, the ratio of the soluble fraction VII_b, decreased strongly (VII_i/VII_b ≈ 1); this observation led us to assume that intermolecular condensations assumed a more important role under these conditions.

Action of Ammonia: Preparation of VIIIs and VIIIi. When reacted with anhydrous gaseous ammonia in dichloromethane, II afforded a soluble fraction VIIIs (70% yield) after filtration and evaporation of the solvent and an insoluble fraction VIIIi, which was not separated from the ammonium chloride. Subsequent aqueous workup of this last mixture led to an insoluble, unmeltable poly(carbosiloxane): elemental analysis of this product revealed the presence only of carbon, silicon, and oxygen, thus demonstrating that all the initially present silicon–nitrogen bonds were hydrolyzed. The yield of the soluble polymer was found to decrease strongly when the reaction time was extended, suggesting that further cross-linking occurred slowly, even at room temperature, probably as a consequence of transamination involving either silyl-amino groups or disilazane linkages (Scheme VI). A re-

Scheme VII. Hydrolysis of II Affording Disiloxane Bridges via Intramolecular or Intermolecular Condensations



sidual chlorine content of 0.5% was found. Polymer VIIIs was very sensitive to moisture and became gradually insoluble and unmeltable after a few days when kept at room temperature, even under argon, but remained unchanged over several weeks at -20°C . This cross-linking could be ascribed to transamination pathways that might occur very slowly in the solid state, affording trisilylated nitrogen centers (Scheme VI).^{14,15}

IR spectrum of VIIIs displayed the characteristic bands of the disilazane units (3380, 1180, and 980 cm⁻¹).

¹H NMR spectrum (200 MHz) of VIIIs exhibited two broad signals centered at 0.15 and -0.13 ppm, respectively assigned to CH₃Si plus Si–NH protons and Si–CH₂–Si protons (integration ratio 4/2). Broadening of the signals might arise from the quadrupolar effect of nitrogen as well as the complex structure of the polymer. The actual framework of VIIIs is best viewed on the basis of Si–CH₂–Si units linked by SiNSi bridges; a wide range of ring structures could arise from silylamine and silazane condensations, as already depicted in Schemes VI and VII, and intramolecular ring closures might occur as well as intermolecular condensations. This assumption also was supported by the soluble fraction GPC profile, showing a significant molecular weight increase and a stronger polydispersity ($M_n \approx 4120$, $\rho = 8.9$). However, the relatively small M_n value change led us to assume that, under our conditions, intramolecular condensations were predominant, yielding only a weakly cross-linked skeleton for the soluble part. This assumption was in good agreement with the TGA curve, as a low ceramic yield of only 37.5% was obtained upon pyrolysis to 1000°C .

Hydrolysis of II: Preparation of IX. To obtain information on the influence of oxygen upon silicon carbide based ceramics, the chlorinated PCS II was hydrolyzed under acidic conditions. This route was expected to afford introduction of oxygen at known positions, as disiloxane bridges. The obtained poly(carbosiloxane), IX, was a brown solid, soluble in organic solvents (98% yield according to eq 6, Scheme II; softening interval 120–130 $^{\circ}\text{C}$).

The ¹H NMR spectrum of IX (60 MHz) exhibited only a broad signal centered at 0.1 ppm (CH₃) but with an upfield broad hump for the CH₂ protons. The IR absorption $\nu(\text{Si–O–Si})$ overlapped the Si–CH₂–Si deformation band between 1000 and 1050 cm⁻¹, whereas no band corresponding to the remaining Si–Cl bonds was detected. These spectroscopic data led us to assume that most of these bonds have been hydrolyzed. This is corroborated by the low residual chlorine content (1.5%). The GPC curve led to $M_n \approx 2960$ and $\rho = 2.5$; this significant increase

in the \bar{M}_n value suggested that, under our conditions, both intramolecular and intermolecular condensations took place (Scheme VII).

Hydrosilylation Reactions of III. Very little information is available on the microstructure of the free carbon and its influence on the thermochemical properties of the resultant silicon carbide ceramics. Therefore, poly(silapropylene) III appeared as an attractive starting material, from the perspective of preparing preceramic polymers with alternate silicon atoms and methylene groups, as encountered in the case of the Yajima's PCS, but also offering the possibility of increasing the carbon ratio by the creation of hydrocarbon bridges. Thus, hydrosilylation of 1,3-butadiene and divinylbenzene with III was performed at 200 °C in a sealed vessel, in the presence of Speier's catalyst.¹⁷ In both cases, insoluble, unmeltable solids were obtained in 97% yield in the case of X and 96% yield in the case of XI (Scheme III, eqs 7 and 8).

The IR spectrum of X is consistent with IR data reported for the comparable derivative of formula $(\text{Me}_3\text{SiCH}_2\text{CH}_2)_2$.¹⁸ In the case of XI, it can be observed that both weak Si-H and vinyl absorptions remained.

Ceramization of the Poly(carbosilane) Models. The ceramic yields were determined from TGA (Table II). The results are consistent with the branching concept suggested by Schilling, i.e., the more branched the polymer, the better its ability to give a high ceramic yield.^{8,12} Thus, I and II are not good ceramic precursors since they are linear. In the same way, most soluble products afford low ceramic yields since they are only poorly cross-linked. On the contrary, the more highly cross-linked polymers in this series, such as IV_i, V_i, VII_b, and IX, are better precursors. These results show that, in spite of their relative thermal instability, silicon-silicon linkages favored high conversion rates when they are included into strongly cross-linked structures. Similarly, cross-linking of poly(carbosilanes) by disiloxane linkages, as in the case of IX, also provides a convenient route to improve char yields. The presence of disilane bridges has previously been inferred in PCS Mark III, whereas disiloxane bridges are generated during industrial curing treatment in air of the precursor fibers.^{19,20}

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Obviously, poly(carbosilanes) with pendant amino groups offering no ability for branching exhibit a poor aptitude for ceramization (i.e., dimethylamino groups). On the other hand, disilazane or *N*-methyldisilazane bridges lead to better precursors.

Long-chain hydrocarbon bridges are not suitable for preceramic polymers, due to the presence of large-membered rings likely to exhibit a weak thermal stability very similar to that of linear structures, as can be inferred from the TGA results of X and XI. Finally it can be seen that most of the prepared model polycarbosilanes readily afford insoluble and unmeltable cross-linked precursors. This strongly increases the difficulty in separating the salts that are often formed when an aqueous workup has to be avoided.

Conclusions

To study the influence of the chemical composition and cross-linking features of organosilicon precursors on the properties of the ceramics obtained upon pyrolysis, we have synthesized novel functional poly(carbosilanes) with backbones comprising exactly alternate silicon atoms and methylene groups. Thus, cross-linked model ceramic precursors possessing disilane, disilazane, disiloxane, and hydrocarbon bridges were prepared. Their ability to give high ceramic yields according to the kind of chemical bridges and their cross-linking degree was investigated. Information concerning their thermal conversion and the properties of the obtained ceramics will be reported in the following paper.

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Registry No. Ammonia, 7664-41-7; 1,3-butadiene, 106-99-0; divinylbenzene, 1321-74-0.

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