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An Original Route to Poly[silylene-*co*-(2,4-disilapentane-2,4-diyl)] Oligomers, Efficient Precursors of Silicon Carbide-based Ceramics with Variable C/Si Ratios

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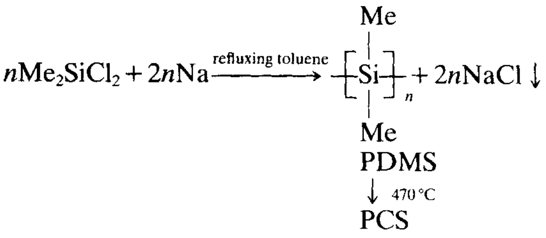
Novel oligomers possessing a backbone formed of ($\equiv Si-CH_2-Si\equiv$) and $(Si)_n$ units were prepared by the copolycondensation of bis(chlorosilyl)methanes and various dichlorosilanes in the presence of sodium, in refluxing toluene. The effect of the respective molar ratios of comonomers on the yields and the structure of the copolymers was investigated. The role of substituents on silicon atoms in the ability of these materials to provide convenient ceramic precursors upon pyrolysis was examined. When $\equiv Si-H$ bonds were present, thermal cross-linking was readily performed and ceramics possessing variable C/Si ratios were prepared.

Keywords: ceramic precursors; poly[silylene-*co*-(2,4-disilapentane-2,4-diyl)]; polycarbosilanes; silicon carbide; fibers; thermal cross-linking

INTRODUCTION

After the pioneering work of Verbeek[1] on the preparation of Si/C and Si/C/N ceramic materials via the pyrolysis of organosilicon polymers, Yajima and his co-workers[2] developed the first routes to silicon carbide-based fibers on an industrial scale. Examples are Nicalon® from Nippon Carbon Co., Japan, and Tyranno® (Ube Industries), from Textron Inc., Lowell, MA, USA. The starting material, poly(dimethylsilylene) (PDMS), was prepared by dechlorination–polycondensation of dimethyldichlorosilane in the presence of sodium, and this polymer was converted into polycarbosilane (PCS) by heating at 400–470 °C under inert gas (Scheme 1).



$$nMe_2SiCl_2 + 2nNa \xrightarrow{\text{refluxing toluene}} \left[\overset{Me}{\underset{Me}{Si}}\right]_n + 2nNaCl\downarrow$$

$$\text{PDMS} \xrightarrow{470\,°C} \text{PCS}$$

Scheme 1

Dramatic changes in the linear backbone of PDMS occurred during this thermolysis, leading to polymers possessing methylhydrosilmethylene linkages $-(MeHSi-CH_2)-$ in a complex framework. These PCSs were successively melt-spun, cross-linked with oxygen from the air, and finally pyrolyzed above 1000 °C to provide ceramic fibers containing silicon carbide, free carbon and silicon oxycarbide. Further, Schilling *et al.*[3] succeeded in a one-step preparation of poly(methylsilylene) (PMS) via dehalo-coupling of $MeHSiCl_2$ using potassium. In their attempts to prepare vinylpolysilane (VPS) from the corresponding dichlorosilanes, these authors showed that the double bonds were consumed. To account for the observed good ceramic yields, they pointed out that their ceramic precursors possessed branched structures and contained Si—H and/or remaining $\geq Si-CH=CH_2$ groups to promote cross-linking upon pyrolysis. Almost simultaneously, Wynne and Rice[4] demonstrated a concept of latent thermal reactivity and stated general requirements for the elaboration of ceramics via pyrolysis of organometallic polymers. Then, various strategies for the preparation of SiC-based cer-

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amics were explored, including synthesis of new polysilanes and polycarbosilanes, chemical modification of polymers and upgrading methods for commercially available precursors.[5-15] Nevertheless, it remains necessary to find new routes to SiC precursors possessing rheological properties suitable for the preparation of ceramic matrix composites (CMCs) and with a better control on their chemical composition. It is worthy of note that Yajima had anticipated in his strategy that the best precursors to form SiC_4 tetrahedra upon pyrolysis should be polycarbosilanes having a main backbone formed of alternating Si and C atoms. Therefore, other routes to such precursors involving polycondensation of chloromethylchlorosilanes via chemical[3] or electrochemical[16] processes have now been investigated. Also, ring-opening polymerization of disilacyclobutanes has emerged as an attractive route to poly(silmethylene) model precursors.[17-19] However, preparation of the starting monomers remains tedious and expensive, so this route does not allow large-scale applications. The direct synthesis of a polycarbosilane, i.e. poly[(diphenylsilylene)-*co*-methylene], recently reported from the polycondensation of diphenyldichlorosilane and dibromomethane in the presence of sodium, might be an alternative to these methods.[20,21] Finally, in order to have a better understanding of structural effects on the conversion of PCS precursors, we reported the first synthesis of a well-defined linear polysilapropylene, $HMe_2Si(CH_2SiMeH)_n$-CH_2SiMe_2H, exhibiting average mass molecular weight values in the same range as Yajima's PCSs.[22] We have shown that its thermal cross-linking proceeded via sila-adamantane-like structures which were assumed to form during the pyrolysis of this class of SiC precursors.[23,24] Following this concept, we described a molecular building-block approach to soluble heterochain copolymers possessing a backbone formed of $\equiv$Si—CH_2—Si$\equiv$ and —$(Si)_n$— sequences, from the cocondensation of symmetrical bis(chlorosilyl)methanes and dichlorosilanes in the presence of sodium.[16c,25] Recently, we reported the use of bis[(chlorohydrogenomethyl)silyl]methane ($ClMeHSiCH_2SiHMeCl$) for the preparation of spinnable SiC precursors containing only a very small excess of free carbon.[26] Since the unique route to this monomer consisted of the condensation of methyldichlorosilane with dibromomethane in the presence of magnesium,[27] we have investigated its synthesis from dichloromethane, which is much cheaper than dibromomethane. Here we report: (1) the synthesis of bis[(chlorohydrogenomethyl)silyl] methane from dichloromethane; (2) the preparation of new poly[silylene-*co*-(2,4-disilapentane-2,4-diyl)] copolymers by cocondensation of this compound with various dichlorosilanes in the presence of sodium; and (3) the conversion and thermal cross-linking of these copolymers into ceramic precursors.

RESULTS AND DISCUSSION

Synthesis of bis[(chlorohydrogenomethyl)silyl] methane

A number of methods for the preparation of functional bis(silyl)methanes have been reported, but derivatives substituted on silicon atoms, such as symmetrical bis[(chlorohydrogenomethyl)silyl]-methane, remained difficult to synthesize.[5,28-33] Although the reaction of magnesium is seldom successful with 1,1-dihalides, the preparation of $CH_2(MgBr)_2$ has been reported by using an amalgam.[34,35] The high cost of dibromomethane and the reluctance to use large amounts of mercury or amalgams in organometallic synthesis led us to investigate the reaction with dichloromethane. Thus, we have succeeded in the first reproducible condensation of dichloromethylsilane with dichloromethane in the presence of magnesium turnings, using THF as the solvent (Eqn [1]).

$$2\ MeHSiCl_2 + CH_2Cl_2 + Mg \rightarrow Cl\text{—}SiMeH\text{—}CH_2\text{—}SiMeH\text{—}Cl + MgCl_2 \quad [1]$$

Besides the expected disilylmethane (35% yield of pure distilled compound), a large amount of undistillable oligomers was also obtained. Thus, the ^1H NMR spectrum of the residue exhibited broad signals at 3.5 ppm (—CH_2—O—) and 1.5 ppm —CH_2—($C\underline{H}_2$)—CH_2, showing that side-reactions involving the solvent had occurred. Indeed, dichlorosilanes had been previously reported to induce cleavage of ethers in the presence of magnesium chloride.[36] In addition, a broad, shielded signal at −0.2 ppm could be assigned to oligomers possessing $\equiv$Si—CH_2—Si$\equiv$ linkages, resulting from the polycondensation of the dichlorosilane with dichloromethane. Finally, narrow peaks at 2.8 ppm showed that Si—CH_2—Cl end-groups were present in some distillation fractions. This observation suggests that the reaction might involve stepwise formation of Grignard reagent, instead of a dimagnesium derivative, from a chloromethyl moiety, and this might be followed by silylation. Then, the disilylated compound might result from the silylation of the intermediate chloromethylsilane, as depicted in Eqns [2]–[4].

$$CH_2Cl_2 + Mg \xrightarrow{THF} [Cl—CH_2—MgCl] \quad [2]$$

$$[Cl—CH_2—MgCl] + MeHSiCl_2 \rightarrow Cl—CH_2—SiMeHCl + MgCl_2 \quad [3]$$

$$Cl—CH_2—SiMeHCl \xrightarrow[McSiHCl_2\text{ (excess)}]{Mg} ClSiMeH—CH_2—SiMeHCl + MgCl_2 \quad [4]$$

Unexpectedly, symmetrical dimagnesium derivatives, e.g. $CH_2(MgBr)_2$, were reported to exhibit a low reactivity towards trimethylchlorosilane.[35] This is in good agreement with the assumption in our case that the condensation might proceed via the monomagnesium derivative of CH_2Cl_2 instead of the dimagnesium derivative.

In attempts to decrease cleavage of the solvent in the presence of dichlorosilane and magnesium salts, various conditions were used. Thus, an unusual procedure consisting of the dropwise addition of THF onto a mixture of the other reactants was followed. Also, the best results were obtained when the temperature was kept below 30 °C during the overall process.

When only magnesium turnings were used, the reaction occurred slowly after the usual activation with iodine, $HgCl_2$ or dibromoethane. In all experiments, it stopped after a few hours, whatever the experimental conditions were (concentration, temperature, excess of metal etc.). When high-purity magnesium powder (Rieke-like magnesium) was used, no appreciable increase in the yield of bis(chlorosilyl)methane was observed. Interestingly, we found that addition of zinc powder (25–50 wt% relative to magnesium) increased the final yield, we also found that this cometal was entirely recovered at the end of the condensation. Indeed, elemental analysis revealed that only $MgCl_2$ and not $ZnCl_2$ was recovered. The exact role of this cometal in the mechanism of the reaction remains unknown. It is apparent from previous work that the mechanism of Grignard reagent formation is radical in nature.[37,38] Various methods for the activation of magnesium have been reported, such as reduction of magnesium salts with electropositive metals, sonication and mechanical activation.[39,40] However, the presence of a zinc trace in magnesium has not been proved to have a marked catalytic effect on Grignard reactions.[38,41]

When zinc alone is used, our results are in good agreement with previous reports recognizing that this metal usually remains inert towards dichloromethane, even as the activated powder.[42] However, the formation of a complex between zinc and dichloromethane in THF has been postulated to account for the methylenation of ketones.[43] Thus, zinc is suggested to clean up the magnesium surface area, mechanically and perhaps to activate it, but occurrence of a redox Mg/Zn couple was not rejected. Other cometals such as aluminum, copper, cadmium or mercury were less efficient or ineffective.

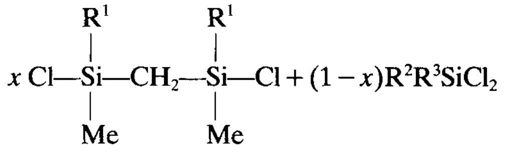
Synthesis of poly[(silylene)-*co*-(2,4-disilapentane-2,4-diyl)]copolymers

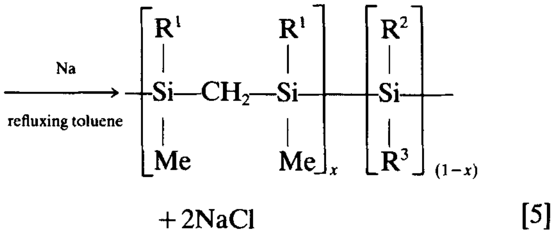
Sodium polycondensation of chlorinated carbosilanes Cl—Me_2Si—$(CH_2)_n$—$SiMe_2$—Cl ($n \geq 1$) has been mentioned in the literature for the preparation of heterochain permethylated homo- and co-polymers,[30,44] but these polymers cannot be regarded as effective silicon carbide precursors since they contain too large an excess of carbon with respect to silicon, as well as a poor capability to cross-link. In contrast, polycarbosilanes possessing ≡Si—H bonds were expected to avoid these drawbacks. Accordingly, we have carried out sodium condensations of mixtures of Cl—MeHSi—CH_2—SiMeH—Cl with Me_2SiCl_2, using increasing molar proportions of this bis(chlorosilyl)methane in refluxing toluene as the solvent. Condensations of Cl—Me_2Si—CH_2—$SiMe_2$—Cl with $MeHSiCl_2$ were also investigated as an alternative route to ≡Si—H— containing copolymers. To extend the field of application of this approach and to obtain ceramics with variable C/Si ratios, copolymers with phenyl, cyclohexyl and n-butyl substituents were prepared as well (Eqn [5]).

Table 1 Poly[silylene-*co*-(2,4-disilapentane-2,4-diyl)] copolymers resulting from the sodium copolycondensation of $(ClMeR^1Si)_2CH_2$ (x) and $R^2R^3SiCl_2$ ($1-x$)

Run[a] no.	R^1	R^2	R^3	x	n^b (mol)	Sol. yield (%)[c]	Insol. yield (%)[d]
1	H	Me	Me	0.05	0.025	32	65
2	H	Me	Me	0.15	0.06	58	30
3	H	Me	Me	0.20	0.066	61	24
4	H	Me	Me	0.25	0.25	75	15
5	H	Me	Me	0.35	0.175	78	14
6	H	Me	Me	0.50	0.25	83	5
7	Me	Me	Me	0.25	0.070	32	53
8	Me	Me	H	0.15	0.086	49.5	5
9	Me	Me	H	0.25	0.10	60	2
10	H	Ph	Me	0.25	0.075	95	4.5
11	H	Ph	Me	0.50	0.15	98	1.0
12	H	n-Bu	Me	0.50	0.235	89	—
13	H	$C_6H_{11}Me$	Me	0.50	0.218	85	5

[a] Reflux time: 24 h. [b] Number of moles of starting (bis)dichlorosilylmethane. [c] Yield of copolymer soluble in toluene. [d] Yield of insoluble copolymer.





$$x\,Cl-\overset{R^1}{\underset{Me}{Si}}-CH_2-\overset{R^1}{\underset{Me}{Si}}-Cl + (1-x)R^2R^3SiCl_2 \xrightarrow[\text{refluxing toluene}]{Na} \left[\overset{R^1}{\underset{Me}{Si}}-CH_2-\overset{R^1}{\underset{Me}{Si}}\right]_x \left[\overset{R^2}{\underset{R^3}{Si}}\right]_{(1-x)} + 2NaCl \qquad [5]$$

$0 \leq x \leq 1$; $R^1 = H, Me$; $R^2 = Me, n\text{-}Bu, c\text{-}Hexyl, Ph$; $R^3 = H, Me$

The results are listed in Table 1. Whereas the PDMS used in the Yajima route ($x=0$, $R^2=R^3=Me$) is a white infusible solid, insoluble in toluene, THF and hydrocarbons, insertion of 2,4-disilapentane sequences in the poly(dimethylsilylene) backbone led to soluble copolymers. After distillation of very small fractions of low-boiling products under high vacuum, gray or

Table 2 SEC results, residual chlorine percentages and char yields for some copolymers

	Soluble copolymer			
Run no.	$\bar{M}_W$	$\bar{M}_w/\bar{M}_n$	Cl (%)	TGA char yield[a] (%)
2	2900	2.7	1.0	2.5
4	5000	3.4	0.5	3.5
6	5600	5.5	1.5	4.0
7	3000	3.0	1.7	7.0
8	3900	3.5	1.5	40.0
9	3500	3.2	1.4	38.0
10	11200	4.9	0.2	11.0
11	25000	8.8	0.2	15.8
12	3200 (broad, major)	1.7	0.5	2.8
	70000 (weak, minor)	1.9	—	—
13	1600 (broad, major)	2.0	0.2	4.5
	50000 (weak, minor)	1.6	—	—

[a] At 950 °C.

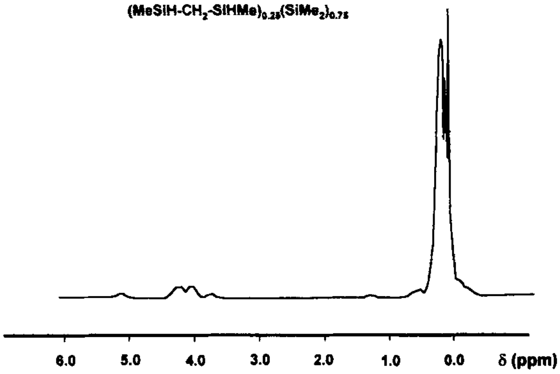


Figure 1 250-MHz ^1H NMR spectrum of copolymer obtained in run 4.

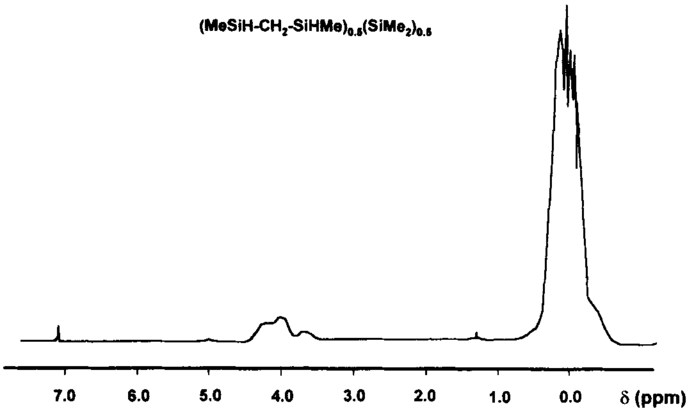


Figure 2 250-MHz ^{1}H NMR spectrum of copolymer obtained in run 6.

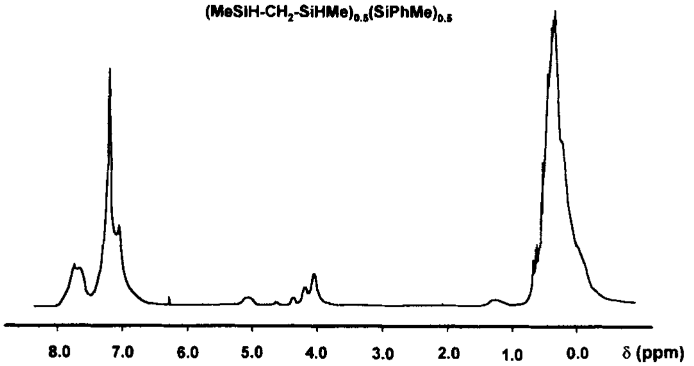


Figure 3 250-MHz ^{1}H NMR spectrum of copolymer obtained in run 11.

gray–bluish translucent materials possessing low viscosities which became fluid upon warming were obtained. Usually, SEC profiles of these products exhibit a main broad hump and overlapping narrow peaks corresponding to low-mass oligomers. In addition, they contain very low percentages of residual chlorine (Table 2).

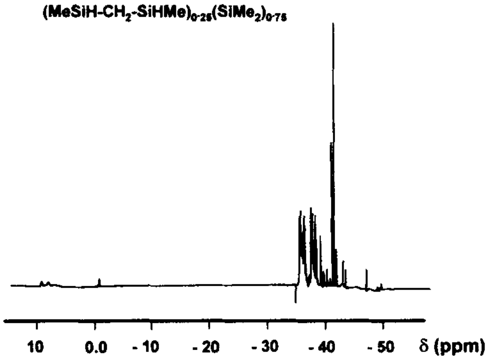


Figure 4 39.7-MHz ^{29}Si NMR spectrum of copolymer obtained in run 4.

Condensations involving Cl—MeHSi—CH$_2$—SiMeH—Cl (runs 1–6) afforded oligomers which were soluble in the usual organic solvents (toluene, THF, heptane) even though low proportions of this comonomer were used. Yields of these soluble materials readily increased when x values increased. For instance, yields increased from 32% when $x = 0.05$ to 75% when $x = 0.25$. Insoluble solids were also formed but only in low

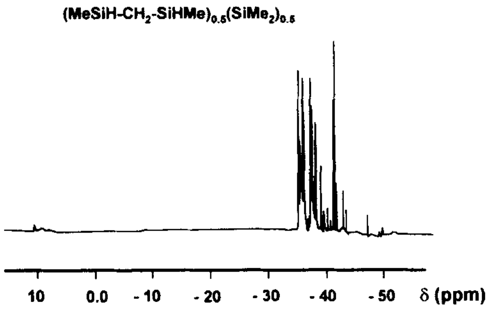


Figure 5 39.7-MHz ^{29}Si NMR spectrum of copolymer obtained in run 6.

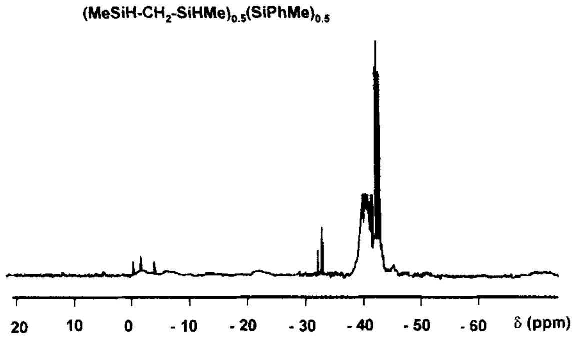


Figure 6 39.7-MHz ^{29}Si NMR spectrum of copolymer obtained in run 11.

yields, except for the lowest value of x (run 1). This might be accounted for by the formation of long —(Me$_2$Si)$_n$— chains since only a low percentage of starting disilylmethane was used. These observations as a whole suggest that both comonomers exhibit no marked tendency to self-condense under the conditions used, but that they readily give cross-coupling condensations.

Physicochemical data corroborated these assumptions. Thus, ^{1}H NMR spectra of copolymers obtained from the condensation of bis[(chlorohydrogenomethyl)silyl]methane and, respectively, dimethyldichlorosilane (Fig. 1, $x = 0.25$; and Fig. 2, $x = 0.5$) or methylphenyldichlorosilane (Fig. 3, $x = 0.5$) exhibited two overlapping broad signals centered at 0.0 ppm (≡Si—CH$_3$ protons) and −0.05 ppm (shoulder, ≡Si—CH$_2$—Si≡ protons). Another broad signal in the range 4.0–

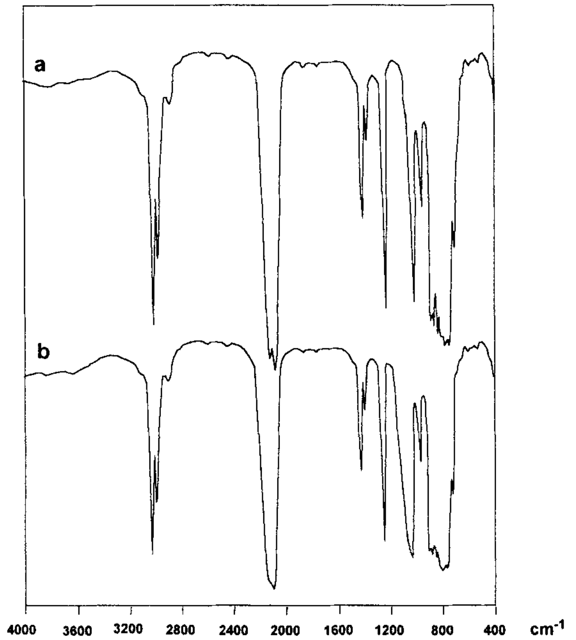


Figure 7 IR spectra of copolymer obtained in run 6: (a) neat product; (b) after exposure in air (2 h).

Table 3 Thermolysis of copolymers

Run no.	Gas volume[a] (ml g^{-1})	Low-boiling fraction yield (%)	Insoluble PCS yield (%)	Soluble PCS yield (%)	Softening temp. range (°C)	PCS no.
2	90	15	0.0	48.0	115–120	14
2	100	16.0	2.0	46.0	140–150	15
2	120	19.0	3.0	44.0	>250	16
4	95	10.0	7.0	46.0	160–170	17
4	105	22.0	11.0	42.0	200	18
4	112	12.5	10.0	41.0	>250	19
4	156	10.0	45.0	—	>250	20
5	80	16.0	2.0	47	120	21
5	93	16.2	2.0	44.0	160	22
6	85	17.0	4.0	49.0	180–190	23
7	15	45	5	—	—	24
8	60	18	50.0	29	>250	25
9	88	7.0	62.5	—	>250	26
10	30	30	14	35	170–180	27
10	35	38	5.2	45	250	28
11	30	2.0	1.0	60	110–120	29
11	32	0.0	27	53	150–160	30
11	37	0.0	27	50	220–230	31

[a] Volume of evolved gases (ml per g of starting copolymer).

Table 4 SEC and TGA results of selected PCSs

Soluble PCS no.	$\bar{M}_W$	$\bar{M}_w/\bar{M}_a$	Ceramic yield (%)
14	4100	3.4	44.0
15	5400	3.8	62.0
16	41000	17	84.0
17	12300	8	73.0
18	74250	31	78.0
19	160000	58	87.0
22	32500	13	71.0
23	8500	6.5	74
27	7700	4	—
28	6000	3	77.0
29	15300	5.2	60.0
30	4000	3.2	71.0
31	4300	2.4	75.0

4.2 ppm corresponds to $\equiv$Si—H protons. As expected, the $\equiv$SiCH/$\equiv$SiH integration ratio is closely dependent on the x value. Usually, this ratio was about 10% higher than the calculated value for each copolymer, showing that a small amount of $\equiv$Si—H bonds was consumed. ^{29}Si NMR spectra (INEPT) of these copolymers (Figs 4, 5 and 6) exhibit two main broad signals in the range of -35, -37 ppm and -42, -45 ppm, respectively assigned to the expected —CH_2—SiMeH—Si$\equiv$ and $\equiv$Si—$SiMe_2$—Si$\equiv$ nuclei. The intensities of the signals are dependent on the values of x. Very weak signals in the range of 10–11 ppm and 22–24 ppm were assigned to remaining —CH_2—SiMeH—Cl and Si—$SiMe_2$—Cl terminals respectively. When x increased, i.e. when the proportion of the monomer containing $\equiv$Si—H bonds increased, additional relatively weak signals in the -40 ppm region were assigned to branched silicon atoms —CH_2—$SiMeSi_2$ resulting from the substitution of $\equiv$Si—H bonds.

Condensation using Cl—Me_2Si—CH_2—$SiMe_2$—Cl instead of Cl—MeSiH—CH_2—SiMeH—Cl afforded lower yields of soluble products (Table 2, runs 7–9). Moreover, runs 4 and 7 show that for the same x value ($x = 0.25$), oligomers with an appreciably lower M value were obtained. Very likely, the higher reactivity of Me_2SiCl_2 with respect to that of the permethylated disilylmethane is responsible for the formation of large —$(Me_2Si)_n$— chains and therefore for the observed decrease in solubility. When $MeHSiCl_2$ was used as comonomer instead of Me_2SiCl_2 (runs 8 and 9), the overall yield was appreciably lower: thus the yields of soluble polymers were lower though only small amounts of insoluble polymers were formed. This result is supported by the evolution of gases resulting from disproportionation reactions of $MeHSiCl_2$ (M. Birot, J. P. Pillot and J. Dunoguès, unpublished results) leading to the formation of silanes (mainly $MeSiH_3$ and Me_2SiH_2). The fact that IR spectra of insoluble fractions in runs 1 and 7 and PDMS look very similar is in good agreement with the assumption that these insoluble copolymers contain mainly —(Me_2Si)— units: thus, only very weak bands at 1040 and 1350 cm^{-1} assigned to Si—CH_2—Si moieties[45–47] were observed, the main difference consisting of the presence of a relatively weak band at 2100 cm^{-1} in the case of the insoluble material from run 1, showing that only a small proportion of chlorinated disilylmethane reacted. Moreover, the residual chlorine content of soluble oligomers was significantly higher than in other runs. GC analysis of the distilled fraction showed that an appreciable amount of unreacted disilylmethane was recovered when Cl—Me_2Si—CH_2—$SiMe_2$—Cl was used as a comonomer. These results lead us to infer that Cl—Me_2Si—CH_2—$SiMe_2$—Cl exhibits a lower ability to polycondense than its $\equiv$Si—H-containing homologue. Therefore, this monomer might behave as a chain-length limiter in sodium-induced polycondensations.

The ^{1}H NMR spectra of copolymers prepared from dichloromethylsilane (runs 8 and 9) show that $\equiv$Si—H bonds were consumed to a large extent since $\equiv$SiCH/$\equiv$SiH ratios were considerably higher than the expected values (20–40% of $\equiv$Si—H bonds disappeared). Accordingly, the corresponding copolymers should possess branched structures containing $\equiv$Si—$Me\underline{Si}Si_2$ units. This is corroborated by the presence of ^{29}Si NMR signals at -80 ppm ($Me\underline{Si}Si_3$), as previously reported for the homopolymer obtained from $MeSiHCl_2$.[48] These oligomers are very air-sensitive. Thus, the IR spectrum of the neat copolymer in run 6 exhibited a narrow absorption band at 1030–1040 cm^{-1} but, after exposure in air for a few hours, a shoulder at 1060 cm^{-1}, assigned to the formation of Si—O—Si bonds, was observed (Fig. 7). This is consistent with the fact that Si—O—Si and Si—CH_2—Si moieties give very close IR absorption bands.[49,50] Thus, it has previously been reported that polycarbosilanes which contain oxygen exhibit broadening of the IR absorption band at 1040 cm^{-1}.[2c,i] In spite of their low weight-average molecular mass values (Table 2), they gave higher char yields than other copolymers, probably because they possess a branched structure. Indeed, polysilanes possessing ≡Si—H bonds have been reported to undergo cross-linking reactions under various conditions.[12,48,51]

In the same way, condensations involving Cl—MeHSi—CH_2—SiMeH—Cl and $MePhSiCl_2$ (runs 10 and 11) resulted in very high yields of soluble copolymers, possessing relatively high weight-average molecular masses, whereas only very small amounts of insoluble products were formed. Similarly, n-$BuSiMeCl_2$ and c-$HexSiMeCl_2$ (runs 12 and 13) provided high yields of soluble materials. SEC profiles of these oligomers exhibit three main regions: a narrow peak for low-mass compounds, a broad hump corresponding to the main part of the product and a weak hump corresponding to high-mass polymers, i.e. $M_W = 70\,000$ and 50 000 respectively. IR spectra of these materials are in good agreement with the expected structures. So, they exhibit absorption bands at 2100 cm^{-1} (SiH), 1030 cm^{-1} (≡Si—CH_2—Si≡ deformation) and 1350 cm^{-1} (CH_2 deformation in ≡Si—CH_2—Si≡).

Thermal cross-linking of poly[silylene-*co*-(2,4-disilapentane-2,4-diyl)] copolymers: synthesis of novel polycarbosilanes (PCSs)

As expected, most of these oligomers afforded low char yields upon direct pyrolysis because they possess linear backbones. Owing to the presence of ≡Si—H bonds, they were expected to be cross-linked according to various routes. Thus, we have shown that they could be converted into soluble solid polycarbosilanes (PCSs) upon progressive heating under inert gas at atmospheric pressure. Results of the thermolysis are given in Table 3 and weight-average molecular masses of selected soluble PCSs are listed in Table 4.

Upon heating at 350–500 °C under argon, ≡Si—H-containing oligomers led to the formation of gases and refluxing low-boiling compounds. This shows that splitting of the backbone first occurred, even though it seems reasonable to assume that a small amount of low-mass oligomers were present in the starting materials. Then, the temperature inside the flask progressively increased while the reflux went down. Simultaneously, the viscosity of the residue increased. From these observations it can be inferred that, above 320–350 °C, condensation of the initially formed oligomers progressively affords solid, cross-linked polymers. To obtain precursors with high char yields upon pyrolysis while retaining solubility in the usual organic solvents and good melt-spinning ability, the reaction was conveniently controlled, for given values of x, by measuring the volume of gas evolved (Table 3). Copolymers containing phenyl groups underwent cross-linking reactions as well (Table 3, PCSs 27–31) but, when $x = 0.25$ (PCSs 27 and 28), large amounts of distillable products were obtained. From Tables 3 and 4, it can be demonstrated that ≡Si—H bonds play a crucial role in these transformations:

(1) For a given series of starting oligomers, the thermolysis became easier when x values increased (Table 3, PCSs 14–23). Thus, for similar gas evolutions, products possessing both higher melting point and M_W values (i.e., more cross-linked structures) were obtained when x values were high. Simultaneously, char yields increased.

(2) In the case of the thermolysis of Si—H-rich copolymers (runs 8 and 9), the starting compounds were found to be thermally unstable since it was not possible to control the reaction: they rapidly led to insoluble and infusible products.

(3) On the other hand, the permethylated copolymer (copolymer from run 7) was far more stable under similar conditions. Heating for 18 h at 400 °C led to very weak gas evolution. Only splitting of the backbone occurred, leading to distillable carbosilanes, while no substantial cross-linking, providing an increase in average molecular mass, was observed.

IR, ^1H NMR and on-line GC–MS characterizations showed that the isolated low-boiling-point fractions were formed of complex mixtures of carbosilanes (Fig. 8). ^1H NMR spectra of the as-obtained soluble PCSs exhibited very broad signals at 0.0 ppm (≡Si—CH_3), −0.05

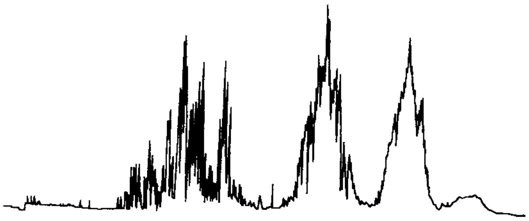


Figure 8 GC profile of low-boiling-point carbosilanes.

Table 5 Elemental compositions of the pyrolytic residues for some selected polycarbosilanes (atomic percentages)

	Ceramic		
PCS no.	C (%)	Si (%)	O (%)
15	58	37	5
23	55	41	4
25	45	48	7
28	63	30	7

($\equiv$Si—CH_2—Si$\equiv$) and 3.8–4.5 ppm ($\equiv$Si—H). An appreciable decrease of the $\equiv$SiH/$\equiv$CH ratio showed that $\equiv$Si—H bonds were consumed during the thermolysis. ^{29}Si NMR spectra of these materials exhibited broad signals. Generally, a marked decrease of $\equiv$Si—($\underline{Si}Me_2$)—Si$\equiv$ and —CH_2—$\underline{Si}$MeH—Si signals between -37 and -42 ppm was observed, whereas an increase of signals near 0 ppm (SiC_4) occurred, suggesting that novel $\equiv$Si—CH_2—Si$\equiv$ sites were formed, resulting from insertion of methylene groups into $\equiv$Si—Si$\equiv$ bonds (Kumada's rearrangement) or from condensation between $\equiv$Si—H and $\equiv$Si—CH_3 groups.[6] This was corroborated by an increase in IR bands at 1040 and 1350 cm^{-1}. For poorly cross-linked polymers, i.e. compounds exhibiting low softening temperatures, the conversion of (CH_3)Si—Si$\equiv$ moieties into $\equiv$Si—CH_2—Si$\equiv$ linkages was not complete. This was checked by IR (ν_{Si-Si} at 450–400 cm^{-1} and UV spectroscopy (Si—Si absorptions at 240–300 nm).

These results as a whole corroborate the suggestion that the conversion of PDMS into PCS (at temperatures ranging from 400 to 470 °C)[2] proceeds via two main pathways: (1) cleavage of Si—Si bonds, leading to the formation of $\equiv$Si—CH_2—Si$\equiv$ and $\equiv$Si—H linkages; (2) cross-linking involving $\equiv$Si—H bonds. Conversely, in our strategy, the thermal cross-linking takes place more readily at lower temperatures: 350–400 °C instead of 450–470 °C in the case of the synthesis of a Mark I PCS from PDMS,[2] since $\equiv$Si—H bonds are present in the starting oligomers.

Pyrolysis of polycarbosilanes

Ceramization of PCSs was performed under argon at 950 °C. The elemental compositions of the residues are given in Table 5. For low values of x, the C/Si ratio of the ceramic is close to that of Nicalon® fiber (ceramic from PCS 15), as previously reported.[53,54] As could be predicted, the carbon content goes down when x increases (ceramic from PCS 23). In the case of the pyrolysis of PCS 23, the percentage of silicon is higher than that of carbon, as previously reported for PMHS.[48] The oxygen content is relatively high, corroborating the idea that contamination of the precursor occurred. Finally, materials containing phenyl groups (i.e. ceramic from PCS 28) were useful for studying the microstructure and the role of free carbon in silicon carbide-based ceramics.[53]

CONCLUSION

An original route to 2,4-dichloro-2,4-disilapentane, consisting of the condensation of dichloromethane and dichloromethylsilane in the presence of magnesium and zinc as cometal, is reported. This monomer was used in sodium-induced polycondensation reactions with various dichlorosilanes, yielding novel oligomers possessing —(MeHSi—CH_2—SiMeH)— and —(SiR_2)— units in their backbone. To study the effect of substituents on silicon atoms upon the ability of these oligomers to give useful ceramic precursors, copolymers were also synthesized starting from 2,4-dichloro-2,4-dimethyl-2,4-disilapentane. Thus, it was shown that copolymers possessing $\equiv$Si—H bonds could be thermally cross-linked prior to pyrolysis to give fusible, soluble preceramic polymers. In addition, this route offers great potential in the preparation of ceramics possessing tunable C/Si ratios: thus, precursors possessing phenyl substituents give carbon-rich silicon carbide-based ceramics whereas those possessing a high proportion of $\equiv$Si—H bonds yield ceramics with relatively low percentages of carbon.

EXPERIMENTAL

Solvents

Pentane and toluene were distilled over sodium and lithium aluminum hydride just before use; THF was distilled on sodium/benzophenone or naphthalene/sodium, and ether on $LiAlH_4$. Solvents were stored in the dark under argon.

Reagents

Dichloromethane was kept over molecular sieves. The chlorosilanes were distilled from magnesium turnings just before use.

Characterizations

Weight-average molecular masses of the polymers were determined by size exclusion chromatography (SEC) with five Microstyragel columns (porosity range 10^2, 5×10^2, 10^3, 10^4 and 10^5 Å) calibrated with polystyrene standards; THF was the eluent at a flow rate of 1 ml/min^{-1}. The detection system was a Waters Associates differential refractometer R401. ^{29}Si (39.76 MHz) and ^{1}H (250 MHz) NMR spectra were obtained from Bruker AC 200 and AC 250 spectrometers in $CDCl_3$ or C_6D_6 solutions, with TMS ($\delta = 0$ ppm) as the external standard. INEPT conditions were used in the first case.[54] Mass spectra (MS) were obtained from an AG-F VG Micromass spectrometer (70 eV). IR spectra in the range 4000–6000 cm^{-1} were recorded on a Perkin–Elmer 1420 spectrophotometer (neat product between NaCl plates) and Perkin–Elmer 983 equipped with a Perkin–Elmer 3600 data station to obtain spectra in the region 4000–200 cm^{-1} (neat product between TlBrI plates). UV spectra were recorded on a Cary 219 spectrometer in a quartz cell (10 mm) with dry degassed cyclohexane as the solvent. Thermogravimetric analyses (TGA) were achieved with a TGS2 Perkin–Elmer thermobalance from samples of about 10 mg in a platinum crucible (heating rate 5 °C min^{-1} from 40 to 950 °C, argon flow rate 60 ml/min^{-1}). Elemental analyses of polymeric materials were carried out by the Service Central d'Analyse du CNRS, BP 22, F-69390 Vernaison, France. Elemental analyses of ceramics were performed by electron-probe microanalysis (EPMA; Camebax-75). The hydrogen content was not estimated by this technique.

Preparation of 2,4-dichloro-2,4-disilapentane from dichloromethane

A four-necked, round-bottomed flask (2 l Sovirel®) was equipped with a thermometric well, a dropping funnel, a reflux condenser (circulation of decalin cooled at −10 °C) connected to a drying column, an inlet for the inert gas purge (nitrogen or argon) and a mechanical stirrer. After flame-drying and purging with argon, magnesium turnings (48.64 g, 2 mol), zinc powder (20 g, 0.3 mol), CH_2Cl_2 (85 g, 1 mol) and $HMeSiCl_2$ (575 g, 5 mol; large excess) were introduced into the flask. The mixture was kept at room temperature for 2 h. THF (750 ml) was then added dropwise under vigorous stirring, rapidly resulting in the appearance of a black color while the temperature slowly went up. The mixture temperature must not exceed 30 °C. Then, a grey color indicated that MgCl was formed. When the addition of the solvent was complete (over a period of approx. 18 h), the mixture was stirred for 48 h at 20–25 °C. Excess of $HMeSiCl_2$ and THF were then distilled off under vacuum at room temperature and condensed into two liquid-nitrogen-cooled traps. The gray, solid residue was dissolved in dry pentane (1 l) and vigorously stirred for 36 h under argon. The solution was filtered off under argon and the solid washed three times with pentane. After combination of the filtrates and evaporation of the solvent, a colorless liquid (59 g, 0.337 mol) was obtained on fractioning distillation, corresponding to the expected product, HMeSiCl—CH_2—SiHMeCl. Yield 34%, b.p.$_{42\,\mathrm{Torr}}$ 66 °C. The decoupled ^{29}Si NMR spectrum of this compound exhibits two narrow peaks of the same intensities at 8.8 and 8.9 ppm (presence of two diastereoisomers). The following coupling constants were found: $^1J_{SiH} = 230$ Hz, $^2J_{SiCH3} = 7.5$ Hz, $^2J_{SiCH2} = 9.5$ Hz, $^3J_{SiH} = 3$ Hz. The ^{1}H NMR spectrum showed two doublets centered at 0.24 and 0.25 ppm (CH_3Si) ($^3J_{SiH} = 3.1$ Hz); CH_2 protons exhibited two overlapping signals (two diastereoisomers): (a) 0.14 ppm (broad triplet, A_2X_2 spectrum, $J_{AX} = {}^3J_{SiH} = 3.4$ Hz); (b) 0.10–0.19 ppm (ABX_2 spectrum, $J_{AB} = 15$ Hz, $J_{AX} \approx J_{BX} = {}^3J_{SiH} \approx 3.3$ Hz); 4.84 and 4.85 ppm, overlapping multiplets (SiH protons).

Preparation of 2,4-dichloro-2,4-dimethyl-2,4-disilapentane

$(ClMe_2Si)_2CH_2$ was prepared from $(Me_3Si)_2CH_2$, Me_3SiCl, and $AlCl_3$ according to a previously reported route.[55]

Preparation of poly[silylene-*co*-(2,4-disilapentane-2,4-diyl)] copolymers

Into a two-necked round-bottomed flask equipped with a pressure-equalizing dropping funnel, a reflux condenser fitted with a $CaCl_2$ column, and a circulation of dry argon, were introduced the solvent (120 ml) and the sodium (4.8 g, 0.2 mol, slight excess) (small pieces). The flask was immersed in an oil bath maintained at 120–130 °C. The molten sodium was finely dispersed upon vigorous magnetic stirring. Then the mixture of dichlorosilane and bis(chlorosilyl)-

methane (overall molar fraction: 0.1 mol) was added dropwise and the reaction mixture progressively turned midnight blue. Reflux and stirring under argon were maintained for 24 h. After cooling (under argon) the solid and liquid fractions were decanted and separated by filtration under a dry inert atmosphere. The blue solid was washed three times with toluene, filtered off, then submitted to methanolysis (because of the presence of remaining sodium) and finally hydrolyzed under acidic conditions. The remaining white or gray solid was separated by filtration, washed with acetone, then ether, and finally dried under vacuum (1 Torr) at 100 °C for several hours. The organic fractions were combined and the solvent was evaporated under vacuum. Finally, crude copolymers were heated at 100 °C/1 Torr to remove low-boiling products.

Thermal cross-linking of poly[silylene-*co*-(2,4-disilapentane-2,4-diyl)] copolymers

The copolymers were introduced under argon flow into a three-necked 250-ml quartz flask equipped with a quartz thermometric well, an argon inlet and a condenser with a quartz nozzle fitted to a bubbler connected with a gas meter. Thermolysis was performed by immersion of the vessel in a fluidized sand bath at the chosen temperature. The increase of the temperature inside the flask as well as the volume of evolved gas were checked. At 300–350 °C white vapors generally appeared and a colorless liquid refluxed while considerable emission of gas was observed. Progressively the reflux and the emission of gas decreased. When the thermolysis was stopped, the vessel was purged with argon and cooled under argon flow. The residue consisted of a yellow solid and a thin supernatant viscous layer. After addition of pentane, stirring for a few hours and filtration to remove any insoluble material, pentane was evaporated under vacuum and the crude material devolatilized at 100 °C/1 Torr for several hours.

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