

Synthesis of disilylmethanes and polysilacarbosilanes, precursors of silicon carbide-based materials¹

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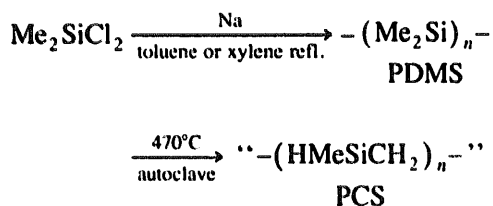
Abstract

Using a new procedure, substituted disilylmethanes have been prepared from chlorosilanes, dichloromethane, and magnesium in tetrahydrofuran. Bis(chlorosilyl)methanes can be used as comonomers for the synthesis of polysilacarbosilanes, which are transformed into polycarbosilanes, precursors of silicon carbide.

Keywords: Disilylmethane; Bis(chlorosilyl)methane; Ceramic precursor; Polysilacarbosilane; Polycarbosilane; Silicon carbide

1. Introduction

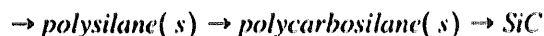
After the pioneering work by Verbeek and coworkers [1–3], who reported the generation of silicon carbide and silicon carbide nitride-based materials from preceramic polymers, Yajima and coworkers [4] developed a strategy to allow the industrial preparation of SiC fibers [5], involving preparation of polycarbosilane (PCS) precursors from polydimethylsilane (PDMS) according to the following scheme [4]:



The PCSs obtained are spun, then cured with oxygen from air, and finally pyrolyzed at 1200–1300°C to provide "SiC" fibers containing, besides silicon car-

bide, some silicon oxycarbide and free carbon. The route

di (or poly-) chlorosilane(s)



has been used by many workers and the results widely reviewed [6]. Despite numerous proposed modifications (mainly related to the nature and mode of synthesis of polysilanes or their conversion into PCSs), and although some direct approaches to PCSs have been reported from tetramethylsilane [4] or, more recently, from chloromethylsilanes through chemical [7–10] or electrochemical [11–13] processes, the Yajima route remains the accepted means of producing satisfactory "SiC" fiber precursors.

Nevertheless, this strategy, which leads to the commercially available Nicalon [5,14] or Tyranno [5,15] fibers, has some drawbacks: the PDMS resulting from the polycondensation of dimethyldichlorosilane is an insoluble solid which is converted into the corresponding PCS only with difficulty. Moreover, the structure of the formed PCS is complex and not well defined [16]. To obtain a better understanding of the conversion of PCS precursors into the corresponding SiC-based materials, we had envisaged a synthesis of a well-defined linear polysilapropylene [HMe₂Si(CH₂SiMeH)_nCH₂SiMe₂H] [17]. Furthermore, we thought that it might be

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possible to prepare a soluble, modified PDMS by introducing Si-CH₂ sequences into the polysilane backbone through co-condensation of Me₂SiCl₂ and ClR₂-SiCH₂SiR₂Cl (R = H, alkyl, or aryl group) in the presence of sodium. We expected that the resulting PSCS would be easily separable from the formed salts without hydrolysis, and consequently would have a very low oxygen content. These PSCSs, representing a partially transformed, soluble PDMS, were expected to undergo rearrangement into PCSs more easily than the usual one.

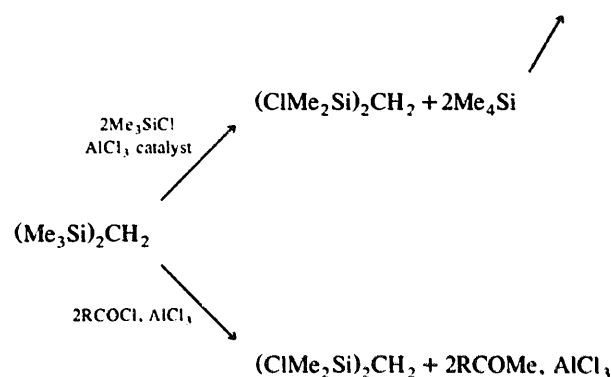
Bis(chlorosilyl)methanes, and especially ClMeH-SiCH₂SiHMeCl, were previously prepared from dichlorosilanes, dibromomethane, and magnesium [18]. We have investigated their preparation from dichloromethane, which is cheaper than dibromomethane, and report: (i) the synthesis of bis(chlorosilyl)methanes from dichloromethane; (ii) the preparation of some polysilacarbosilanes by co-condensation of dichlorosilanes and bis(chlorosilyl)methanes in the presence of sodium; and (iii) some properties of the PCSs obtained by heating the corresponding PSCSs.

2. Results and discussion

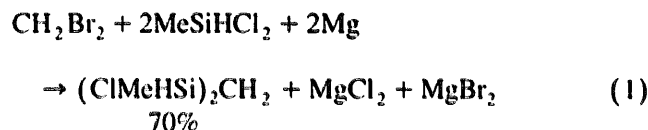
2.1. Synthesis of disilylmethanes

Various routes have been proposed for the synthesis of disilylmethanes. Unfortunately, most of these are not convenient or not simple enough to prepare bis(chlorosilyl)methanes. Thus, the coupling of chloromethylchlorosilanes with dichlorosilanes generally leads to oligomers [19,20], and the synthesis of bis(chlorosilyl)methanes requires the preliminary preparation of the corresponding hydrogenosilanes, followed

by subsequent halogenation of the Si-H bonds, or reactions involving bis(trimethylsilyl)methane [21,22]:



Among the other routes to disilylmethanes, it must be noted that electrochemical synthesis, efficient for obtaining bis(trimethylsilyl)methane [23] from dichloromethane and trimethylchlorosilane, cannot be extended to the preparation of bis(dimethylchlorosilyl)methane, since Me₂SiCl₂ and CH₂Cl₂ exhibit close reduction potentials. At this time, the unique practical route for preparing (ClMeHSi)₂CH₂ is that proposed by Cooke et al. [18]:



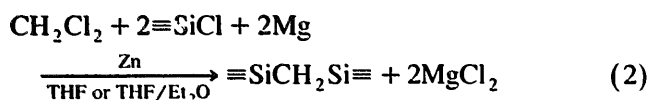
The cost of dibromomethane prompted us to investigate the reaction with dichloromethane, since it had been shown that silylation of this compound with Me₃SiCl was possible using HMPA as solvent [24]. Owing to our reluctance to use this solvent, which is highly carcinogenic [25], we decided to re-investigate the condensation of mono- or dichlorosilanes with dichloromethane in the presence of magnesium. Fair to

Table 1
Disilylmethanes from chlorosilanes, dichloromethane, and magnesium

Entry	Starting chlorosilane (mass (g))	CH ₂ Cl ₂ (g)	Mg (g)	Zn (g)	THF (ml)	Reaction temperature (°C)	Reaction time (h)	Disilylmethane (mass (g))	Yield/CH ₂ Cl ₂ (%)	B.p. (°C Torr ⁻¹)
1	Me ₃ SiCl (25)	8.5	4.9	5.2	100	40	48	(Me ₃ Si) ₂ CH ₂ (7.2)	45	132/760
2	Me ₂ SiHCl (36)	8.5	4.9	3	200	30	24	(Me ₂ HSi) ₂ CH ₂ (9.4)	71	98/760
3	MeHSiCl ₂ (1150)	170	97.3	40	1500	20	48	(ClMeHSi) ₂ CH ₂ (104.3)	30	66/42
4	PhMe ₂ SiCl (40)	8.5	4.9	13	100	40	90	(PhMe ₂ Si) ₂ CH ₂ (10.1)	35	115/0.5
5	ViMe ₂ SiCl (30)	8.5	4.9	4	100 ^a	40	48	(ViMe ₂ Si) ₂ CH ₂ (5.2)	28	75/30
6	PhMeHSiCl (35)	8.5	4.9	5.2	150	40	60	(PhMeHSi) ₂ CH ₂ (16.8)	65	126/1
7	PhHSiCl ₂ (35)	4.3	2.5	2.6	50	40	72	(ClPhHSi) ₂ CH ₂ (10.5)	71	81/0.1
8	EtH ₂ SiCl (19)	8.5	4.9	5.2	180	30	48	(EtH ₂ Si) ₂ CH ₂ (5.2)	39	128/760
9	ViH ₂ SiCl (22)	8.5	4.9	5.2	180	40	48	(ViH ₂ Si) ₂ CH ₂ (1.5)	11	40/30

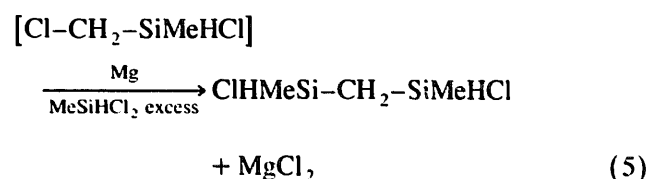
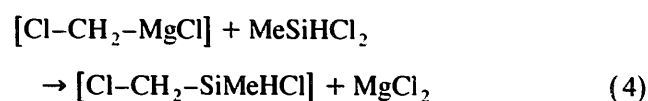
^a THF/Et₂O 60:40.

good yields were obtained using an unusual experimental procedure; in which the solvent (THF or THF/Et₂O) was progressively added to a stirred mixture of the reactants. However, the presence of zinc (25–100 wt.% relative to magnesium) was necessary to perform the reaction conveniently, although the zinc was entirely recovered at the end of the operation (Eq. (2)). The results are summarized in Table 1.



The reaction is slow and side reactions occur when the chlorosilane is too reactive; mainly ring-opening of THF or further reaction of the disilylmethane, as observed for (PhMe₂Si)₂CH₂ where the formation of (PhMe₂Si)₃CH was noted in some experiments. Mixtures of THF/Et₂O were used to minimize these side reactions. It must be emphasized that the reaction proceeds with both hydrido-chlorosilanes and phenylchlorosilanes. In the latter case phenyl groups can be replaced by chlorine atoms [26], and the SiCl bonds formed subsequently reduced to Si–H ones, yielding precursors of ceramics with a low free carbon content [27]. The chloride (ClMeHSi)₂CH₂ was readily reduced to (H₂MeSi)₂CH₂ by LiAlH₄ in 72% yield. Unfortunately, (ClMe₂Si)₂CH₂ cannot be prepared conveniently in this way from Me₂SiCl₂, which reacts with THF, but it was finally obtained from (Me₃Si)₂CH₂ [22] in 87% yield. In the case of MeSiHCl₂, although the expected (ClMeHSi)₂CH₂ is isolated in only fair yields, the process remains competitive because of the very low cost of methylene chloride. Besides the expected disilylmethane (35% yield of pure distilled compound in the best runs), a large amount of undistillable oligomers was also obtained. Thus, the ¹H NMR spectrum of the residue exhibits broad signals near 3.5 ppm (–CH₂–O–) and 1.5 ppm (–CH₂–(CH₂)–CH₂), showing that side reactions involving the solvent occurred. Indeed, dichlorosilanes had previously been reported to induce cleavage of ethers in the presence of magnesium chloride [28]. In addition, a broad, shielded signal at –0.2 ppm could be assigned to oligomers possessing ≡Si–CH₂–Si≡ linkages, resulting from the polycondensation of the dichlorosilane with methylene chloride. The appearance of narrow peaks at 2.8 ppm showed that Si–CH₂–Cl end-groups were present in some distillation fractions. This observation suggests that the reaction may involve the stepwise formation of a Grignard reagent from a chloromethyl moiety, followed by silylation, instead of generation of a dimagnesium derivative. Then, the disilylated compound would result from silylation of the intermediate chloromethylsilane, as depicted in Eqs. (3)–(5). Unexpectedly, symmetrical dimagnesium derivatives, e.g. CH₂(MgBr)₂, were found to exhibit a low reactivity towards trimethylchlorosilane

[29]. This is in good agreement with the assumption that the condensation may proceed via the monomagnesium derivative of CH₂Cl₂ rather than the dimagnesium derivative.



In attempts to limit the cleavage of the solvent by dichlorosilane in the presence of magnesium salts, various conditions were tried. An unusual procedure, involving dropwise addition of the solvent to the mixture of other reactants, was found to be effective, and the best results were obtained when the temperature was kept below 30°C throughout the process.

Except for the experiments in the presence of HMPA, which applied only to the formation of (Me₃Si)₂CH₂ [24] and which cannot be extended to MeSiHCl₂ because the latter undergoes an immediate disproportionation in the presence of HMPA [30], these results provide the first examples of silylation of methylene chloride by organomagnesium intermediates. Although some hypotheses have been formulated [31], the role of zinc has not yet been clearly elucidated. Under our experimental conditions, use of activated magnesium and/or addition of activated zinc accelerates the reaction but does not significantly improve the final yields. When magnesium turnings were used alone, reaction occurred slowly after the usual activation with iodine, HgCl₂, or dibromoethane. In all cases it stopped after a few hours, whatever the experimental conditions (concentration, temperature, excess of metal, etc.). When high purity magnesium powder (Rieke-like magnesium [32]) was used, no appreciable increase in the yield of bis(chlorosilyl)methane was observed. Interestingly, we found that though addition of zinc powder (25–50 wt.% relative to magnesium) increased the final yield, this co-metal was entirely recovered at the end of the condensation. Indeed, elemental analysis of the salts revealed that only MgCl₂ was formed and no ZnCl₂. The exact role of this co-metal in the reaction remains unknown. It is apparent from previous work that the mechanism of Grignard reagent formation is, at least partially, radical in nature [33,34]. Various methods for the activation of magnesium have been reported, such as reduction of magnesium salts with electropositive metals, or use of ultrasonic or mechanical activation [32,35]. However, the presence of a trace of zinc in the magnesium has not

Table 2
Polysilacarbosilanes from $x(\text{ClMeHSi})_2\text{CH}_2$ and $(1-x)\text{Me}_2\text{SiCl}_2$

Entry	x	Mol ^a	Reaction time (h)	Overall yield (%)	Soluble grease (%)	Grease/insoluble (%)
10	0.05	0.50	24	100	32	31/69
11	0.15	0.33	24	95	58	63/37
12	0.15	0.40	24	95	58	68/32
13	0.25	0.40	24	87	63	77/23
14	0.50	0.50	26	100	90	90/10

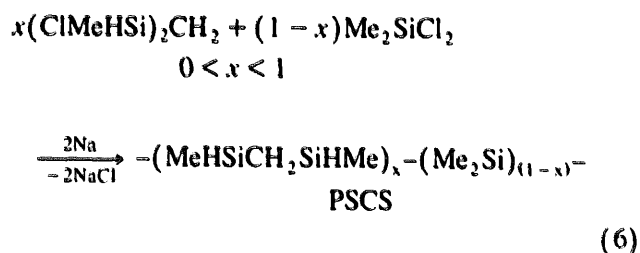
^a Total moles of starting silanes $(\text{ClMeHSi})_2\text{CH}_2 + \text{Me}_2\text{SiCl}_2$.

been found to have a marked catalytic effect on the Grignard reactions [34,36].

When zinc is used alone, our results are in good agreement with previous reports that this metal usually remains inert towards methylene chloride, even as the activated powder [37]. However, formation of a complex between zinc and dichloromethane in THF has been postulated to account for the methylenation of ketones [38]. Thus it was suggested that the zinc mechanically cleans up the magnesium and possibly activates the magnesium surface, but formation of a redox Mg/Zn couple could not be ruled out. Other co-metals such as Al, Cu, Cd, or Hg proved less efficient or wholly ineffective.

2.2. Synthesis of Polysilacarbosilanes

With the aim of introducing Si-CH₂ linkages into the polysilane backbone, we examined the co-polycondensation of bis(chlorosilyl)methanes with dichlorosilanes. Since our main objective is the synthesis of model PCS precursors, most of our studies have involved the preparation of copolymers from Me₂SiCl₂ and (ClMeHSi)₂CH₂ [39]. In the presence of sodium the reaction occurs in refluxing toluene (Eq. (6)). The results are summarized in Table 2.



The PSCSs are generally gray-blue greases that become fluid and translucent on warming, and they are accompanied by insoluble white solids. Average molecular weights \bar{M}_n of the soluble PSCSs are in the range 900–1100, and the polydispersity index Q has a value of 3–6. It can be seen that the reproducibility is rather good (entries 11 and 12), and increasing x favors the formation of the desired soluble fraction. The formula

given for PSCS in Eq. (6) only refers to the number of Si-CH₂-Si and Si-Si linkages and does not take into account the distribution of these bonds along the chain of the polymer. However these moieties have been unambiguously identified by IR, UV, and NMR spectroscopy. From ¹H NMR data, it was established that the ratio between -MeHSiCH₂SiHMe- and -Me₂Si- sequences corresponds relatively well with the chosen value of x , and that the Si-H bonds did not react significantly during the course of the polycondensation. Some chlorine remains in the PSCSs, but generally less than 1 wt.%. Preliminary attempts with $x > 0.50$ showed that the PSCSs formed were insufficiently polycondensed to be used as satisfactory SiC precursors.

Some other PSCSs were prepared similarly, either by replacing (ClMeHSi)₂CH₂ with (ClMe₂Si)₂CH₂, Me₂SiCl₂ with MeSiHCl₂, or by adding a small amount of MeViSiCl₂ to Me₂SiCl₂. From these results (Table 3) the following conclusions can be drawn.

(i) The substrate (ClMe₂Si)₂CH₂ is less reactive than (ClMeHSi)₂CH₂, and acts as a chain-growth limiter in the polycondensation of Me₂SiCl₂ (entry 15, 37% of low-boiling products). Thus the extent of insertion of SiCH₂Si sequences into the PSCS backbone is reduced.

(ii) Replacing Me₂SiCl₂ by MeSiHCl₂ (entry 16) results in a partially branched PSCS, owing to the participation of Si-H bonds in the condensation [40]. The large difference in reactivity between the two chlorosilanes confirms that (ClMe₂Si)₂CH₂ does not allow a high degree of polycondensation. Thus, the polymer is branched but not highly condensed, and this could explain the increase in the amount of the soluble fraction as well as the increase in the ceramic yield.

(iii) When vinyl groups are introduced (entries 17 and 18), thermal hydrosilylation must be taken into account (formation of ≡Si-CH₂CH₂Si≡ and ≡Si-CH(CH₃)Si≡ sequences).

2.3. Synthesis of polycarbosilanes

In the case of PSCS, the ceramic yields of the soluble greases are low (less than 15% at 1000°C) and those of the insoluble species slightly higher (around 20%). This

Table 3
Polysilcarbosilanes from $x(\text{ClMeRSi})_2\text{CH}_2$ and $(1-x)\text{MeR}'\text{SiCl}_2$

Entry	R (mass (g))	R' (mass (g))	x	Sodium (g)	Solvent (mass (g))	Reaction time (h)	Overall yield (%)	Soluble grease (g)(yield (%))	Low b.p. products (g)	Insoluble fraction (g)	Residual Cl (%)	Ceramic yield (%)
15	Me (14.3)	Me (38.7)	0.25	14.1	tol (87)	24	75	6.9 (26)	10	2.81	—	—
16	Me (17.4)	H (29.7)	0.25	16.6	tol (160)	24	85	16.94 (76)	1.44	0.8	1.6	38
17	H (4.32)	Me (54.8) Vi (7.05)	0.05	25.3	tol/THF (132/19.25)	30	91	14.7 (47)	0.3	13.3	< 0.1	10.8
18	H (8.64)	Me (96.74) Vi (28.2)	0.05	50	tol/THF (264/38.5)	30	91	28.41 (45)	0.17	29.18	< 0.1	14.8

is due to some linearity in our PSCSs, as well as to their low molecular weights and low inherent reactivity, and shows that cross-linking is necessary to obtain satisfactory ceramic yields [41]. Consequently, their structures were not investigated in detail and we preferred to study the polycarbosilanes resulting from their thermolysis, since these were expected to be suitable precursors for silicon carbide-based materials. Thus we were able to thermolyze our PSCSs at 270–420°C, whereas PDMSs require the use of an autoclave at 470°C or heating at 500–550°C if they are to be converted into spinnable PCSs. The results are summarized in Table 4.

Most of our studies were devoted to PSCSs from $(\text{ClMeHSi})_2\text{CH}_2$ and Me_2SiCl_2 [39]. Measurements of the volume of the gases evolved per gram of initial PSCS allowed the thermolysis to be monitored, but entries 19–21 indicate that control is difficult. The Si–H bonds play a major role in the process induced by thermolysis since they cause cross-linking and subsequently an increase of the ceramic yield. Thus, when $-\text{MeSiH}-$ units were present (from MeHSiCl_2), no soluble fraction was isolated, even after thermal treatment at 350°C (entry 23). Similarly, thermal branching

(involving perhaps hydrosilylation) involving Si–H bonds was fast under our reaction conditions when $-\text{HMeSiCH}_2\text{SiMeH}-$ units were present (entries 24 and 25), whereas cross-linking was unimportant in the absence of Si–H bonds, and the ceramic yield decreased sharply (entry 22). In the former case good control of the branching seems very difficult to achieve.

The isolated low-boiling products consists of a complex mixture of carbosilanes. The average molecular weights \bar{M}_n and polydispersity values Q of soluble PCSs increase with increasing temperature and duration of thermolysis increase. \bar{M}_n is in the range 1200–1600, while Q has a value of 3–4. When \bar{M}_n is greater than 2500, the value of Q is 10–15. A softening temperature in the range 200–250°C corresponds to $2500 < \bar{M}_n < 2900$, the polydispersity index Q varying between 4.5 and 14. The values are not accurate because the reproducibility of the thermolysis experiments is not very precise. The same variation in reproducibility was observed in our study of the Yajima processes [42].

The intensity of the IR band at 1400 cm^{-1} (δCH_3) relative to that of the band at 1350 cm^{-1} (ωCH_2) increases during the course of thermolysis, but the

Table 4
PCSs obtained by thermolysis of PSCSs

Entry	PSCS no. ^a (mass (g))	Temperature of the bath (°C)	Reaction time (h)	gas (ml) per gram PSCS	Low b.p. (g)	Insoluble fraction (g)	Soluble PCS (g)(yield (%))	Softening temperature (°C)	Ceramic yield at 1000°C (%)
19	12 (12.65)	400	12.2	75	0.7	2.1	5.0 (39)	185	—
20	13 (15.0)	400	17.0	82	—	2.6	2.5 (17)	> 250	87
21	13 (17.0)	400	18.0	156	1.7	7.6	—	> 250	90
22	15 (6.9)	450	36.0	—	1.2	0	2.0 (29)	< 20	—
23	16 (10.6)	350	1.2	88	0.7	6.6	—	> 250	88
24	17 (8.75)	430	2.0	36	1.8	4.6	—	> 250	72
25	18 (12.7)	270	1.0	~ 0	—	12.5	—	> 250	18

^a The numbers correspond to the entries in Tables 2 and 3.

conversion of Si–Si linkages into Si–C–Si moieties is not complete, as confirmed by IR ($\nu(\text{Si–Si})$ at 450–400 cm^{-1}) and UV (Si–Si absorption at 240–300 nm) spectroscopy.

3. Experimental section

3.1. Solvents

Pentane and toluene were distilled just before use; THF was distilled over sodium/benzophenone or naphthalene–sodium, ether over LiAlH_4 , and HMPA over CaH_2 . Solvents were stored in the dark under dry argon.

3.2. Reagents

Methylene chloride (Aldrich) was kept over molecular sieves. Most of the chlorosilanes used, which were distilled from magnesium turnings just before use, were generous gifts from Rhône-Poulenc Co. Low-purity grade magnesium and zinc were used.

3.3. Characterization

Average number molecular weights of the polymers were determined by size exclusion chromatography (SEC) with five Microstyrigel columns (porosity range 10^2 – 10^5 Å) calibrated with polystyrene standards; THF was used as the eluent at a flow rate of 1 ml min^{-1} . The detection system was a Waters Associate differential refractometer R401.

The ^1H (200 MHz), ^{29}Si (39.76 MHz), and ^{13}C (50.3 MHz) NMR data were recorded on a Bruker AC 200 spectrometer, in CDCl_3 or C_6D_6 solutions. Chemical shifts were measured relative to TMS ($\delta = 0$ ppm). ^{29}Si coupling constants were determined by use of the IN-EPT pulse sequence or SPT technique. For $(\text{HR}_2\text{Si})\text{CH}_2$ compounds, separate signals can generally be observed for each diastereoisomer; decoupling experiments in ^1H NMR showed that for the methylene and SiH protons, ABX_2 and A_2X_2 spectra can be assumed for the *meso* and the *racemic* forms respectively. The following abbreviations are used: d, doublet; n, nonuplet; s, singlet; sx, sextuplet; t, triplet; tt, triplet of triplets, m, multiplet; q, quintuplet.

Mass spectra (MS) were obtained with an AG-F VG Micromass spectrometer (70 eV).

IR spectra in the range 4000–600 cm^{-1} were recorded on a Perkin-Elmer 1420 (neat sample between NaCl plates). A Perkin-Elmer 983 spectrophotometer equipped with a Perkin-Elmer 3600 data station was used for spectra in the region 4000–200 cm^{-1} (neat sample between TlBr plates).

UV spectra were recorded on a Cary 219 spectrometer for samples in a quartz cell (1 cm) in dry, degassed cyclohexane.

Thermogravimetric analyses (TGA) were performed with a TGS2 Perkin-Elmer thermobalance on approximately 10 mg samples in a platinum crucible: heating rate 5°C min^{-1} from 40 to 950°C , argon flow rate 60 ml min^{-1} .

Elemental analyses were carried out by the Service Central d'Analyse du CNRS, BP 22, F-69390 Vernaison, France.

3.4. Preparation of disilylmethanes from dichloromethane

Into a three-necked, round-bottomed flask equipped with a magnetic stirrer, a thermometer, a pressure-equalizing dropping funnel, and a reflux condenser filled at the top with a CaCl_2 tube, were successively introduced magnesium turnings, zinc powder, dichloromethane, and the chlorosilane. THF was added dropwise at the temperature indicated in Table 1. The reaction mixture became gray as the MgCl_2 progressively separated. After the end of the reaction the low-boiling products were distilled off and trapped under vacuum. The residual gray solid was extracted with pentane (3×50 ml) under argon, and the disilylmethanes separated by distillation from the initial low-boiling or pentane fractions. Table 1 summarizes the reaction conditions and results.

Some reactions involving "activated" Zn (treated with 3% aq. HCl, distilled water, anhydrous EtOH, and then dried under vacuum in a desiccator containing P_2O_5) or activated Mg did not significantly improve the yields of $(\text{Me}_2\text{Si})_2\text{CH}_2$ from Me_3SiCl and methylene chloride. Various experiments involving use of ether, 1,2-dimethoxyethane, DMF, or tetraglyme instead of THF, and Al, Cu, Cd, or Hg instead of Zn were not really successful, and the best results were observed when THF was added to the stirred mixture of the reactants.

$(\text{ClMe}_2\text{Si})_2\text{CH}_2$ was prepared from $(\text{Me}_2\text{Si})_2\text{CH}_2$, Me_3SiCl , and AlCl_3 according to the route proposed by Sakurai and coworkers [22]. Subsequent reduction of $(\text{ClMe}_2\text{Si})_2\text{CH}_2$ by LiAlH_4 in ether offered a better route to $(\text{HMe}_2\text{Si})_2\text{CH}_2$ (98%). $(\text{H}_2\text{MeSi})_2\text{CH}_2$ was also obtained by reduction of $(\text{ClHMeSi})_2\text{CH}_2$ with LiAlH_4 in Bu_2O (72%) according to a commonly used experimental procedure.

3.5. Physicochemical data of the synthesized disilylmethanes

Except for $(\text{HClPhSi})\text{CH}_2$, $(\text{H}_2\text{ViSi})_2$, $(\text{H}_2\text{EtSi})_2$, and $(\text{HMePhSi})_2$, the properties of the disilylmethanes are

summarized in Ref. [43]. However, characteristic physicochemical data are given here for each product.

3.5.1. Bis(trimethylsilyl)methane

IR (cm^{-1}): 1355 (SiCH_2Si); 1250, 840, 755 (SiMe_3). ^1H NMR (ppm): -0.36 , s, 2H, SiCH_2Si ; 0.04 , s, 18H, 2SiMe_3 . ^{29}Si NMR: 0.30 , $^2J(\text{SiCH}_3) = 7.3$ Hz, $^2J(\text{SiCH}_2) = 8.6$ Hz. ^{13}C NMR: 1.55 (CH_3), 4.5 (CH_2), $^1J(\text{CH}_3) = 118.2$ Hz, $^1J(\text{CH}_2) = 108.7$ Hz, $^3J(\text{CHSiCH}) \sim 2$ Hz. MS (m/z): 145 ($\text{C}_6\text{H}_{17}\text{Si}_2^+$), 73 ($\text{C}_3\text{H}_9\text{Si}^+$).

3.5.2. Bis(dimethylsilyl)methane

IR: ~ 2100 (Si-H); 1355 (SiCH_2Si); 1250 (SiMe_2). ^1H NMR: -0.31 , t, 2H, SiCH_2Si , $^3J(\text{CH}_2\text{SiH}) = 3.8$ Hz; 0.08 , d, 12H, 2SiMe_2 , $^3J(\text{CH}_3\text{SiH}) = 3.7$ Hz; 4.17 , n, 2H, 2SiH . ^{29}Si NMR: -15.82 , $^1J(\text{SiH}) = 183.2$ Hz, $^2J(\text{SiCH}_3) = 7.0$ Hz, $^2J(\text{SiCH}_2) = 8.7$ Hz, $^3J(\text{SiCSiH}) = 3.2$ Hz. ^{13}C NMR: -1.76 (CH_3), $^1J(\text{CH}_3) = 119.3$ Hz, $^2J(\text{CH}_3\text{SiH}) = 7.8$ Hz; -1.1 (CH_2); $^1J(\text{CH}_2) = 112.4$ Hz, $^2J(\text{CH}_3\text{SiH}) = 7.8$ Hz, $^2J(\text{CH}_2\text{SiH}) = 7.9$ Hz, $^3J(\text{CHSiCH}) \sim 2.3$ Hz.

3.5.3. Bis(methylchlorosilyl)methane

IR: characteristic absorption bands similar to those for the previous compound. ^1H NMR: 0.21 , s, 2H, SiCH_2Si ; 0.24 and 0.25 , 6H, 2SiMe , $^3J(\text{CH}_3\text{SiH}) = 3.12$ Hz; CH_2 protons: ABX_2 , $\delta_A = 0.10$, $\delta_B = 0.19$, $^2J_{\text{AB}} = 14.5$ Hz, $^3J_{\text{AX}} = 3.1$ Hz, $^3J_{\text{BX}} = 3.3$ Hz; A_2X_2 , $\delta_A = 0.14$, t, $^3J_{\text{AX}} = 3.4$ Hz; $\delta_X = 4.84$ and 4.85 , m, 2H, 2SiH . ^{29}Si NMR: 9.0 and 9.1 , $^1J(\text{SiH}) = 229.6$ Hz, $^2J(\text{SiCH}_3) = 7.5$ Hz, $^2J(\text{SiCH}_2) = 9.5$ Hz, $^3J(\text{SiCH}_2\text{SiH}) = 3.2$ Hz. ^{13}C NMR: 1.8 and 2.0 (CH_3), $^1J(\text{CH}_3) = 122.3$ Hz, $^2J(\text{CH}_3\text{SiH}) = 11.1$ Hz; 6.62 and 6.68 (CH_2), $^1J(\text{CH}_2) = 115.3$ Hz, $^2J(\text{CH}_2\text{SiH}) = 10.8$ Hz, $^3J(\text{CHSiCH}) \sim 1.5$ Hz. MS (m/z): 171 ($\text{C}_3\text{H}_9\text{Cl}_2\text{Si}_2^+$), 157 ($\text{C}_2\text{H}_7\text{Cl}_2\text{Si}_2^+$), 137 ($\text{C}_3\text{H}_{10}\text{ClSi}_2^+$), 93 ($\text{C}_2\text{H}_6\text{ClSi}^+$), 79 (CH_4ClSi^+), 63 (ClSi^+), 43 (CH_3Si^+).

3.5.4. Bis(phenyldimethylsilyl)methane

IR: besides the absorption bands characteristic of SiMe and SiCH_2Si bonds, bands from the phenyl group are present at 3050 , between 2000 and 1800 , and at 1605 cm^{-1} . ^1H NMR: 0.45 , s, 12H, 2SiMe_2 ; 0.49 , s, 2H, SiCH_2Si ; 7.55 – 7.73 , m, 10H, 2Ph. MS (m/z): 284 ($\text{C}_{17}\text{H}_{24}\text{Si}_2^+$), 269 ($\text{C}_{16}\text{H}_{21}\text{Si}_2^+$), 191 ($\text{C}_{10}\text{H}_{15}\text{Si}_2^+$), 135 ($\text{C}_8\text{H}_{11}\text{Si}^+$).

3.5.5. Bis(vinyldimethylsilyl)methane

IR (cm^{-1}): the expected absorption bands at 3050 (Vi), 1355 (SiCH_2Si), 1250 (SiMe) are observed. ^1H NMR: -0.12 , s, 2H, SiCH_2Si ; 0.12 , s, 12H, 2SiMe_2 ; vinyl part: 6H, 2 ViSi, ABC spectrum (12 lines), $\delta_A = 6.20$, $\delta_B = 5.93$, $\delta_C = 5.66$, $J_{\text{AC}} = 20.2$ Hz, $J_{\text{BC}} = 3.9$ Hz, $J_{\text{AB}} = 14.7$ Hz. MS (m/z): 169 ($\text{C}_8\text{H}_{17}\text{Si}_2^+$), 141

($\text{C}_6\text{H}_{13}\text{Si}_2^+$), 129 ($\text{C}_5\text{H}_{13}\text{Si}_2^+$), 85 ($\text{C}_5\text{H}_9\text{Si}^+$), 73 ($\text{C}_3\text{H}_9\text{Si}^+$), 59 ($\text{C}_2\text{H}_7\text{Si}^+$).

3.5.6. Bis(phenylmethylsilyl)methane

IR: this compound exhibits the same characteristic bands as $(\text{PhMe}_2\text{Si})_2\text{CH}_2$, but there is also a ν_{SiH} band at ~ 2100 cm^{-1} . ^1H NMR: 0.25 , d, 6H, 2SiMe , $^3J(\text{CH}_3\text{SiH}) = 3.7$ Hz; CH_2 protons: ABX_2 , $\delta_A = 0.03$, $\delta_B = 0.04$, $^2J_{\text{AB}} = 13.9$ Hz, $^3J_{\text{AX}} = 3.4$ Hz, $^3J_{\text{BX}} = 4.5$ Hz, A_2X_2 , $\delta_A = 0.16$, t, $^3J_{\text{AX}} = 4.1$ Hz; $\delta_X = 4.70$ and 4.71 , m, 2H, 2SiH . ^{29}Si NMR: -16.0 and -15.6 , $^1J(\text{SiH}) = 196.2$. MS (m/z): 241 ($\text{C}_{14}\text{H}_{17}\text{Si}_2^+$), 178 ($\text{C}_9\text{H}_{14}\text{Si}_2^+$), 177, 163 ($\text{C}_8\text{H}_{11}\text{Si}_2^+$), 135 ($\text{C}_8\text{H}_{11}\text{Si}^+$), 121 ($\text{C}_7\text{H}_9\text{Si}^+$).

3.5.7. Bis(phenylchlorosilyl)methane

IR: this compound exhibits the same characteristic bands as $(\text{PhMeSiH})_2\text{CH}_2$, except for the absence of those due to the SiMe bond. ^1H NMR: CH_2 protons, ABX_2 , $\delta_A = 0.61$, $\delta_B = 0.81$, $^2J_{\text{AB}} = 14.2$ Hz, $^3J_{\text{AX}} = 7.4$ Hz, $^3J_{\text{BX}} = 3.6$ Hz; A_2X_2 , $\delta_A = 0.68$, t, $^3J_{\text{AX}} = 3.45$ Hz; $\delta_X = 5.36$ and 5.42 , m, 2H, 2SiH ; 7.1 and 7.4 , m, 10H, 2PhSi. ^{29}Si NMR: 0.57 , $^1J(\text{SiH}) = 237.1$ Hz. MS (m/z): 296 ($\text{C}_{13}\text{H}_{14}\text{Cl}_2\text{Si}_2^+$), 295, 259 ($\text{C}_{13}\text{H}_{12}\text{ClSi}_2^+$), 218 ($\text{C}_7\text{H}_8\text{Cl}_2\text{Si}_2^+$), 217, 183 ($\text{C}_7\text{H}_8\text{ClSi}_2^+$), 155 ($\text{C}_7\text{H}_8\text{ClSi}^+$), 141 ($\text{C}_6\text{H}_6\text{ClSi}^+$), 105 ($\text{C}_6\text{H}_5\text{Si}^+$), 63 (ClSi^+).

3.5.8. Bis(dimethylchlorosilyl)methane

IR: the characteristic SiMe and SiCH_2Si bands are observed. ^1H NMR: 0.21 , s, 2H, SiCH_2Si ; 0.29 , s, 12H, 2SiMe_2 . ^{29}Si NMR: 28.51 , $^2J(\text{SiCH}_3) = 7.0$ Hz, $^2J(\text{SiCH}_2) = 9.2$ Hz. ^{13}C NMR: 4.6 (CH_3); 11.1 (CH_2); $^1J(\text{CH}_3) = 121.1$ Hz, $^1J(\text{CH}_2) = 111.9$, $^3J(\text{CHSiCH}) = 1.5$ Hz.

3.5.9. Bis(methylsilyl)methane

IR: The characteristic SiH , SiMe and SiCH_2Si bands are present. ^1H NMR: -0.32 , q, 2H, SiCH_2Si ; 0.045 , t, 6H, 2SiMe ; 3.98 , sx, 4H, 2SiH_2 ; $^3J(\text{CH}_3\text{SiH}) = 4.15$ Hz, $^3J(\text{CH}_2\text{SiH}) = 4.2$ Hz. ^{29}Si NMR: -36.05 ; $^1J(\text{SiH}) = 186.2$ Hz, $^2J(\text{SiCH}_3) = 7.4$ Hz, $^1J(\text{SiCH}_2) = 8.9$ Hz, $^3J(\text{SiCSiH}) = 4.2$ Hz. ^{13}C NMR: -9.9 (CH_2); -6.3 (CH_3); $^1J(\text{CH}_3) = 121$ Hz, $^1J(\text{CH}_2) = 112$ Hz, $^2J(\text{CH}_3\text{SiH}) = 6.1$ Hz, $^2J(\text{CH}_2\text{SiH}) = 6.5$ Hz, $^3J(\text{CHSiCH}) = 2.25$ Hz. MS (m/z): 103 ($\text{C}_3\text{H}_{11}\text{Si}_2^+$), 102 ($\text{C}_3\text{H}_{10}\text{Si}_2^+$), 89 ($\text{C}_2\text{H}_9\text{Si}_2^+$), 59 ($\text{C}_2\text{H}_7\text{Si}^+$), 43 (CH_3Si^+).

3.5.10. Bis(ethylsilyl)methane

IR: The characteristic SiH and SiCH_2Si bands are present. ^1H NMR: -0.32 , q, 2H, SiCH_2Si ; A_3B_2 spectrum, $\delta_A = 0.95$, $\delta_B = 0.56$, 10H, 2Et, $^3J_{\text{AB}} = 7.8$ Hz; 4.0 , tt, 4H, 2SiH_2 , $^3J[(\text{CH}_3)\text{CH}_2\text{SiH}] = 3.5$ Hz, $^3J[(\text{Si})\text{CH}_2\text{SiH}] = 4.3$ Hz. ^{29}Si NMR: -28.2 ; $^1J(\text{SiH})$

= 187.6 Hz, $^2J(\text{SiCH}_2\text{Si}) = 8.9$ Hz, $^2J(\text{SiCH}_2\text{CH}_3) = 8.2$ Hz, $^3J(\text{SiCH}_2\text{SiH}) = 3.6$ Hz, $^3J(\text{SiCH}_2\text{CH}_3) = 7.2$ Hz. MS (m/z): 131 ($\text{C}_5\text{H}_{15}\text{Si}_2^+$), 103 ($\text{C}_3\text{H}_{11}\text{Si}_2^+$), 75 (CH_7Si_2^+).

3.5.11. Bis(vinylsilyl)methane

This compound was not isolated in a pure state and only identified by IR spectroscopy (presence of vinyl groups, SiH and SiCH₂Si bonds) and mass spectrometry (m/z): 127 ($\text{C}_5\text{H}_{11}\text{Si}_2^+$), 100 ($\text{C}_3\text{H}_8\text{Si}_2^+$), 99, 85, 72.

3.6. Preparation of polysilacarbosilanes

In a two-necked, round-bottomed flask equipped with a pressure-equalizing dropping funnel, a reflux condenser fitted with a CaCl₂ column and a flow of dry argon were introduced the solvent and small pieces of sodium (see Tables 2 and 3). The flask was immersed in a silicone bath maintained at 120–130°C. The molten sodium was finely dispersed by vigorous magnetic stirring, then the mixture of dichlorosilane and bis(chlorosilyl)methane was added dropwise. The reaction medium became pink and then progressively midnight blue. Reflux with stirring under argon was maintained for about 20 h after the addition. After cooling (still under argon), the solid and liquid fractions were separated by centrifugation under argon. The dark blue solid was washed with toluene (3 × 20 ml), separated each time by centrifugation, then treated with methanol (to destroy the remaining sodium) and finally hydrolyzed under acidic conditions. The remaining white or gray solid was filtered off, washed with acetone then ether, and finally dried at 100°C Torr⁻¹ for several hours. The combined liquid fractions were evaporated and finally heated at 100°C Torr⁻¹ to remove the low-boiling products.

The residue consisted of a soluble, often blue-gray grease, which was translucent and fluid at 80–100°C but gelled at room temperature. This soluble greasy fraction was stored in the dark under dry argon. The results are summarized in Tables 2 and 3.

As indicated in Section 2, the PSCSs were identified by: (i) IR, presence of Si–H, SiMe, SiCH₂Si linkages (see above) but also Si–Si bonds (450–400 cm⁻¹); (ii) UV, strong absorption between 240 and 300 nm; (iii) ¹H NMR, the insoluble fraction was not examined but for the soluble grease it was noted that the ratio of the signals assigned to SiMe (SiPh, SiVi), SiH and SiCH₂Si was in good agreement with the value of x (molar fraction of the disilylmethane involved). Thus the value of x determines quite clearly the structure of the PSCSs formed. Besides, no evidence could be found of incorporation of fluorine in the polymers as a result of the degradation of the Teflon®-coated magnetic stirring bars upon prolonged exposure to molten sodium.

3.7. Preparation of polycarbosilanes

PSCSs were introduced under an argon flow into a three-necked 250 ml quartz flask equipped with a quartz thermometer well, an argon inlet and a condenser with a quartz nozzle attached to a bubbler connected with a gasmeter. Thermolysis was performed by immersion of the vessel into a sand bath at the chosen temperature. The effects of variations in temperature and evolution of gas were noted. At 300–350°C white vapors generally appeared, and a colorless liquid refluxed, while a substantial evolution of gas was observed. The rate of reflux and gas evolution decreased. When the thermolysis was stopped, the vessel was purged and cooled under a dry argon flow. The residue consisted of a yellow solid and a viscous liquid. After extraction with pentane under stirring, the solid was separated by filtration and the pentane extract was evaporated then kept at 100°C Torr⁻¹ for several hours to remove all traces of volatile material. Table 4 summarizes the results. Although the Si–Si linkages did not completely disappear, IR and NMR data were similar to those of the Yajima Mark I product [4] (especially in respect to the relative intensity of $\nu_{\text{C-H}}$ and $\nu_{\text{Si-H}}$), and indicate the unambiguous formation of backbones with alternating silicon and carbon atoms.

4. Conclusion

Using a new procedure, symmetrical disilylmethanes with various substituents can be synthesized directly from dichloromethane and dichlorosilanes by coupling with magnesium in the presence of zinc. The solvent (THF) is added to the mixture of the reactants. Polysilacarbosilane copolymers can be prepared from dichlorosilanes and bis(chlorosilyl)methanes by reductive coupling with sodium. The results confirm that our copolymerization strategy allows the synthesis of soluble PCSs at atmospheric pressure without the use of any initiator or additive.

The PCSs resulting from the copolymer process seem as easy to spin as the Yajima Mark I product. From Table 4 it can be noted that the ceramic yields are equivalent or higher than those obtained by Yajima. (approximately 50–60%) [4], even when the polydispersity values Q are high.

Finally, a preliminary X-ray study of the ceramics resulting from the pyrolysis at 1200°C of some of our PCSs [44] indicates that they crystallize at higher temperature than those prepared by the Yajima process, although the latter contain more oxygen. However, as expected after 20 h at 1600°C the spectra become very similar.

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