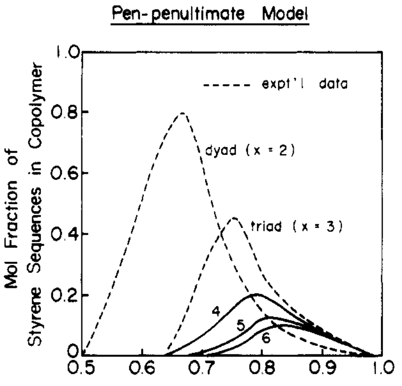

Figure 7. Styrene sequence distribution calculated on the basis of a pen-penultimate model; (- - -) experimental data.

Figure 6 is the distribution calculated by eq 12, where P_{smm} and P_{mmm} were unknown parameters and determined from the experimental fractions of monad and dyad.

3. Pen-penultimate Model. The distribution can be calculated from the following definition and the equations (Figure 7).

$$P_{\mathrm{mmmm}} + P_{\mathrm{mmms}} = 1, \qquad P_{\mathrm{smmm}} + P_{\mathrm{smms}} = 1 \quad (13)$$

$$X(\mathrm{SM}^n\mathrm{S}) = X(\mathrm{S})P_{\mathrm{smmm}}P_{\mathrm{mmmm}}^{\,n-3}(1 - P_{\mathrm{mmmm}}) \qquad (n > 3) \quad (14)$$

These distribution curves, shown in Figures 5-7, clearly reveal that the propagation mechanism for the free radical copolymerization of sulfur dioxide and styrene is not explained by a Markoff chain mechanism, even though the penultimate or pen-penultimate unit effect was taken into consideration for it. In the Markoff chain mechanism, the positions of the peak of the distribution curves are never shifted by a change in the copolymer composition. In other words, as reported by many investigators,[14] the predominant component in the copolymer is always the monad irrespective of the copolymer compositions, and the fraction of longer sequence becomes small with sequence length when the Markoff chain mechanism is operative. It is reconfirmed from the data of the distribution of the styrene sequences that Mayo-Lewis-type propagation is never operative in the present copolymerization.

Registry No. (Styrene)(SO_2) (copolymer), 26779-73-7.

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New Polycarbosilane Models. 1. Poly[(methylchlorosilylene)methylene], a Novel, Functional Polycarbosilane

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ABSTRACT: The aluminium trichloride catalyzed interchange of methyl and chlorine on silicon has been applied for the first time to the polycarbosilane series. Thus, poly[(dimethylsilylene)methylene] ($-(\mathrm{Me_2SiCH_2})_n-$, $\bar{M}_n \simeq 250000$) has been converted into a poly[(methylsilylene)methylene] ($\bar{M}_n \simeq 2300$), the first functional polycarbosilane possessing an unambiguous linear skeleton. The considerable lowering of the average molecular weight, a consequence of the backbone cleavage, was accompanied by the formation of dimethylchlorosilyl groups as the chain terminals. These were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR.

Introduction

Recently, considerable interest has been focused on polycarbosilanes, since Yajima and co-workers demonstrated that these polymers were convenient precursors for silicon carbide fibers.[1] Spinnable polymers were prepared by thermal rearrangement of poly(dimethylsilane), but their structure could not be described accurately by the ideal linear structure $-(\mathrm{MeSiHCH_2})_n-$ which has been originally postulated.[2] More likely, some cyclic framework may arise from side cross-linking reactions proceeding by not yet established mechanisms.[3]

The paucity of information concerning silmethylene polymers prompted us to undertake the synthesis of such derivatives. We report here the preparation and the characterization of the first poly[(methylchlorosilylene)methylene]. Thanks to its highly reactive Si-Cl bonds, it can be regarded as a precursor of a range of novel functional polycarbosilanes.

Results and Discussion

Poly[(dimethylsilylene)methylene] (1) is known to possess an unambiguous linear skeleton and high average molecular weight.[4] This soluble polymer was readily ob-

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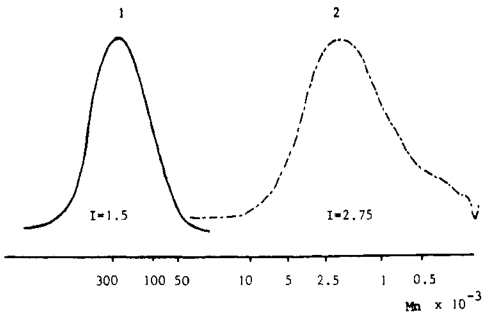


Figure 1. GPC elution curves of polycarbosilanes 1 and 2. Molecular weights are relative to polystyrene standards; I = polydispersity.

tained from 1,1,3,3-tetramethyl-1,3 disilacyclobutane, in high yields, under mild conditions.[5] In order to take advantage of its interesting structure, it seemed logical to carry out chemical modification with the hope of preparing new poly[(methylsilylene)methylene] models. Our strategy was based on the chemoselective conversion of 1 into the corresponding chlorinated polymer 2. Owing to the reactivity of Si–Cl bonds the preparation of new functional polycarbosilanes models should be feasible, as shown in Scheme I.

Scheme I

$$\underset{1}{-(\mathrm{Si(CH_3)_2CH_2})_n-} \rightarrow \underset{2}{-(\mathrm{SiCl(CH_3)CH_2})_n-} \rightarrow -(\mathrm{SiR(CH_3)CH_2})_n-$$

R = H, D, Si<, NHSi<, NHMe, NMe$_2$, etc...

(1) Chlorination of 1. Several routes effecting the conversion of Si–CH$_3$ into Si–Cl bonds have been reported for short chain molecules, but most of them are inapplicable to polymers. In addition, quantitative and selective reactions were needed. In particular, the substitution of two methyl groups per silicon must be avoided.

We anticipated that the action of trimethylchlorosilane in the presence of aluminium trichloride as catalyst[6] would provide the desired polymer under mild conditions, according to eq 1.

$$\underset{1}{-(\mathrm{Si(CH_3)_2CH_2})_n-} \xrightleftharpoons[\mathrm{AlCl_3}]{\mathrm{(CH_3)_3SiCl,\ excess}} \underset{2}{-(\mathrm{SiCl(CH_3)CH_2})_n-} + n\underset{\mathrm{TMS}}{\mathrm{(CH_3)_4Si}} \quad (1)$$

In order to shift the equilibrium, TMS must be removed by distillation. A large excess of trimethylchlorosilane allowed the initial solubilization of 1, and a catalytic amount of AlCl$_3$ (5% by weight relative to 1) was added to this solution, which was then refluxed. Within a few hours, more than 95% of the expected TMS was recovered upon distillation. After filtration and devolatilization under reduced pressure at 100 °C, polymer 2 was obtained in quantitative yield as a brown viscous oil at room temperature, whereas only a trace of low-boiling products (other than TMS) was detected. Product 2 is soluble in polar solvents (ethers, aromatic and chlorinated solvents) but insoluble in nonpolar solvents such as hexane.

Comparison of the GPC curves of polymers 1 and 2 showed a marked decrease of the average molecular weight for the chlorinated polymer, revealing that some of the Si–CH$_2$ bonds also were broken (Figure 1). One can infer that these conversions proceeded according to an electrophilic substitution of methyl groups or SiCH$_2$ moieties on silicon, from trimethylchlorosilane complexed with aluminium chloride.[6] Thus it can be assumed that two reactions converged in the formation of 2 as depicted in Scheme II. The GPC elution profile of poly[(dimethylsilylene)methylene] reacted with Me$_3$SiCl/AlCl$_3$ (Figure 1, curve 2) indicates that the cleavage of the Si–CH$_2$ bonds took place according to a random manner. The calculated ratio of the bonds which were converted into dimethylchlorosilyl chain ends was found to be less than 1:10. Thus, despite the fact that path A was largely predominant, path B resulted in considerable shortening of the chain lengths. The theoretical amount of TMS was not altered by path B which, like path A, produced one TMS molecule per substituted silicon. On the other hand, path B resulted in the formation of additional ClMe$_2$Si– units at the chain terminals, thus slightly increasing the expected final polymer's weight.

Scheme II

$$-(\mathrm{Si(CH_3)_2CH_2})- \xrightarrow[\mathrm{AlCl_3}]{\mathrm{(CH_3)_3SiCl}} -(\mathrm{SiCl(CH_3)CH_2})- + \mathrm{(CH_3)_4Si} \quad (A)$$

$$-\mathrm{CH_2Si(CH_3)_2CH_2}- \xrightarrow[\mathrm{AlCl_3}]{\mathrm{(CH_3)_3SiCl}} -\mathrm{CH_2Si(CH_3)_2Cl} +$$

$$\mathrm{(CH_3)_3SiCH_2}- \xrightarrow[\mathrm{AlCl_3}]{\mathrm{(CH_3)_3SiCl}} 2\text{-}\mathrm{CH_2Si(CH_3)_2Cl} + \mathrm{(CH_3)_4Si} \quad (B)$$

Table I
Infrared Absorption of Polycarbosilane 2

wavenumber, cm^{-1}	assignments
2965 (m)	CH$_3$ stretch (a)
2900 (w)	CH$_2$ stretch (a)
2880 (w)	CH$_3$ stretch (s)
1410 (m)	CH$_3$(–Si) deformation (a)
1350 (m)	(Si)–CH$_2$–(Si) deformation
1260 (s)	CH$_3$–(Si) deformation
1060 (vs)	(Si)–CH$_2$–(Si) deformation
810 (br, vs) 750 (sh)	Si–CH$_3$ rocking
720 (m)	Si–C stretch (a)
660 (m)	Si–C stretch (s)

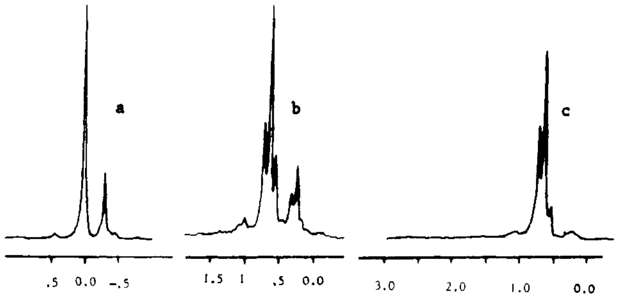


Figure 2. ^{1}H NMR spectra, 60 MHz: (a) starting $-(\mathrm{Me_2SiCH_2})_n-$ (1); (b) 1 after uncomplete reaction time; (c) pure $-(\mathrm{MeSiClCH_2})_n-$ (2).

The ^{1}H, ^{29}Si, and ^{13}C NMR spectra of polymer 2 are given in Figures 2–5 and IR data listed in Table I. As can be seen in Figure 2c, the ^{1}H NMR spectrum (60 MHz) shows characteristic and reproducible signals at 0.71, 0.63, and 0.53 ppm. However, when the reaction did not go to completion, the spectrum exhibited three other signals centered at 0.2 ppm (assigned to –CH$_2$SiMe$_2$– remaining units), the intensities of which decreased during the reaction (Figure 2b). Thus it can be assumed from the NMR results that Si–CH$_2$ cleavage occurred in a chemoselective fashion, since no SiCH$_2$Cl group was observed. Moreover, neither –Si(CH$_3$)Cl$_2$ nor –SiCl$_2$– groups were detected by ^{29}Si NMR, as expected, since the interchange of methyl and chlorine on silicon cannot take place on a –(CH$_3$)SiCl–

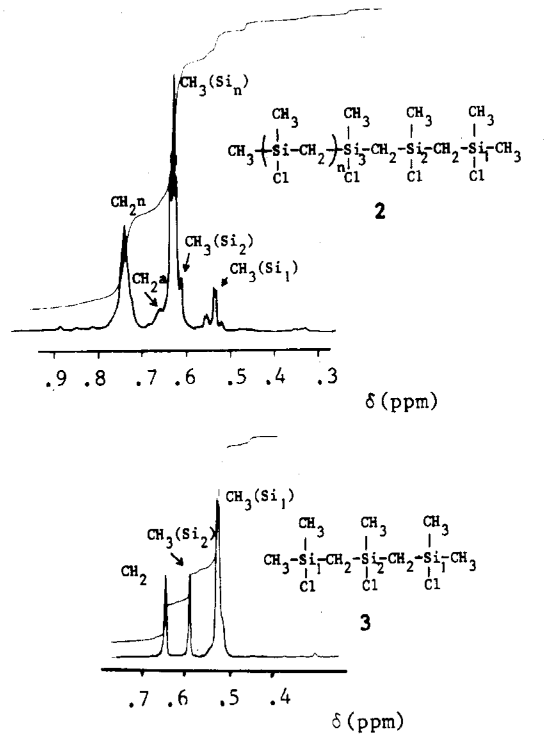


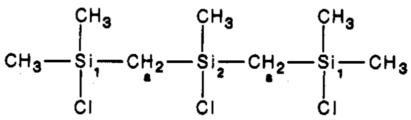
Figure 3. ^{1}H NMR, 200 MHz spectra of polycarbosilanes 2 and 3.

Table II
^{1}H NMR Data, 200 MHz, of Compounds 3–5

compd	chem shifts (solvent, $DCCl_3$), δ (assignments)
3	0.525–0.530 (2s, $CH_3(Si_1)$, 12 H)
	0.59 (s, $CH_3(Si_2)$, 3 H)
	0.65 (s, CH_2(a), 4 H)
4	0.52–0.53 (2s, $CH_3(Si_1)$, 12 H)
	0.605–0.610 (2 s, $CH_3(Si_2)$, 6 H)
	0.66 (br s, CH_2 (a), 4 H)
	0.71 (s, CH_2 (b), 2 H)
5	0.530–0.535 (2s, $CH_3(Si_1)$, 12 H)
	0.610–0.615 (2s, $CH_3(Si_2)$, 6 H)
	0.625–0.630–0.635 (3 peaks (1:2:1 intensities), $CH_3(Si_3)$, 6 H)
	0.660–0.665 (2 s, CH_2 (a), 4 H)
	0.730–0.735 (2s, CH_2 (b), 4 H)
	0.75 (s, CH_2(c), 2 H)

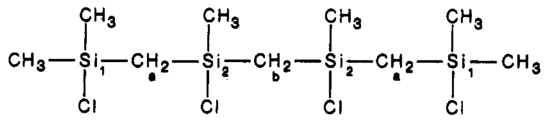
group under our conditions.

The structure of polymer 2 was elucidated from the 200-MHz ^{1}H NMR spectra of short-chain models, i.e., compounds 3, 4, and 5.[7] Assignments of the different



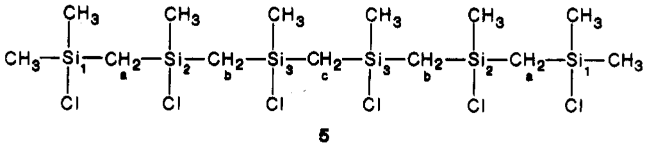
$$\mathrm{CH_3{-}\overset{CH_3}{\underset{Cl}{Si_1}}{-}\underset{a}{CH_2}{-}\overset{CH_3}{\underset{Cl}{Si_2}}{-}\underset{a}{CH_2}{-}\overset{CH_3}{\underset{Cl}{Si_1}}{-}CH_3}$$

3



$$\mathrm{CH_3{-}\overset{CH_3}{\underset{Cl}{Si_1}}{-}\underset{a}{CH_2}{-}\overset{CH_3}{\underset{Cl}{Si_2}}{-}\underset{b}{CH_2}{-}\overset{CH_3}{\underset{Cl}{Si_2}}{-}\underset{a}{CH_2}{-}\overset{CH_3}{\underset{Cl}{Si_1}}{-}CH_3}$$

4



$$\mathrm{CH_3{-}\overset{CH_3}{\underset{Cl}{Si_1}}{-}\underset{a}{CH_2}{-}\overset{CH_3}{\underset{Cl}{Si_2}}{-}\underset{b}{CH_2}{-}\overset{CH_3}{\underset{Cl}{Si_3}}{-}\underset{c}{CH_2}{-}\overset{CH_3}{\underset{Cl}{Si_3}}{-}\underset{b}{CH_2}{-}\overset{CH_3}{\underset{Cl}{Si_2}}{-}\underset{a}{CH_2}{-}\overset{CH_3}{\underset{Cl}{Si_1}}{-}CH_3}$$

5

signals of these compounds are given in Table II. One observes that all the methylene protons exhibit singlets for derivatives 3 and 4. In the case of 5, the methylene

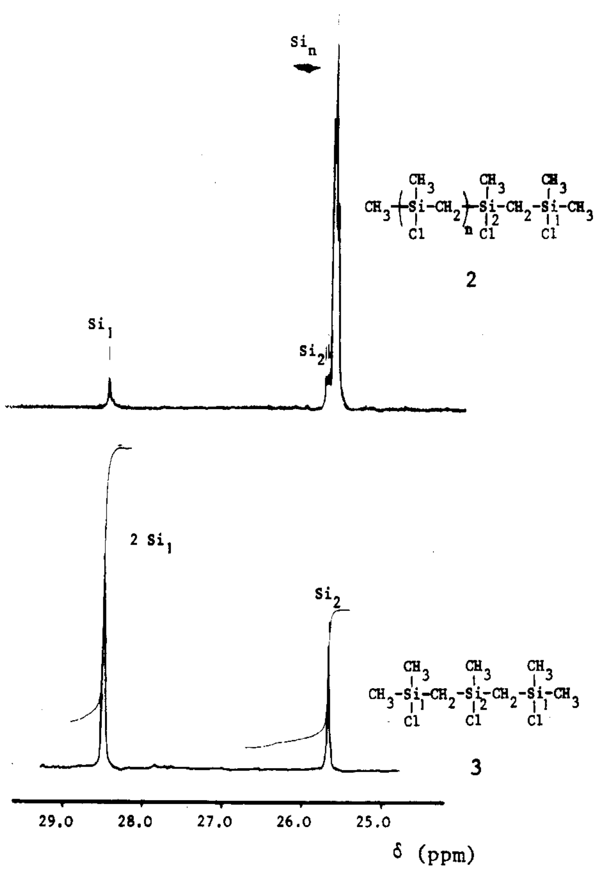


Figure 4. ^{29}Si NMR spectra of polycarbosilanes 2 and 3.

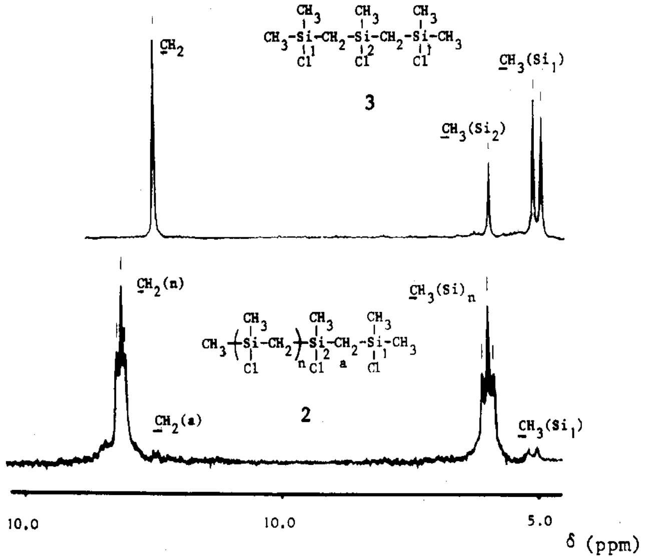
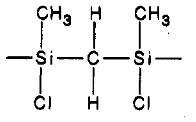


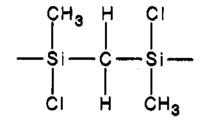
Figure 5. ^{13}C broad band decoupling NMR spectra of polycarbosilanes 2 and 3.

protons all exhibited two very close singlets with the exception of CH_2 (c), which gave a broad singlet. As in the case of polymer 2, no AB spectrum was observed for these protons. This result suggests that compounds 2–5 contain only syndiotactic sequences.



$$\mathrm{{-}\overset{CH_3}{\underset{Cl}{Si}}{-}\overset{H}{\underset{H}{C}}{-}\overset{CH_3}{\underset{Cl}{Si}}{-}}$$

isotactic sequence

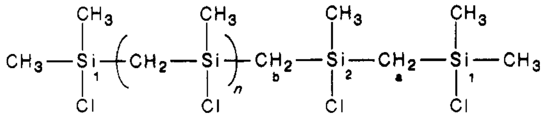


$$\mathrm{{-}\overset{CH_3}{\underset{Cl}{Si}}{-}\overset{H}{\underset{H}{C}}{-}\overset{Cl}{\underset{CH_3}{Si}}{-}}$$

syndiotactic sequence

However, short-chain models contain mixtures of all possible configurational sequences, since their synthetic

Table III
^{1}H NMR Spectrum, 200 MHz, of Poly[(methylchlorosilylene)methylene]



$$CH_3-\underset{Cl}{\overset{CH_3}{\underset{1}{Si}}}-\left(CH_2-\underset{Cl}{\overset{CH_3}{Si}}\right)_n-\underset{b}{CH_2}-\underset{Cl}{\overset{CH_3}{\underset{2}{Si}}}-\underset{a}{CH_2}-\underset{Cl}{\overset{CH_3}{\underset{1}{Si}}}-CH_3$$

chem shifts (solvent, $DCCl_3$) δ (assignments)
0.53–0.54 (2s, weak, $CH_3(Si_1)$)
0.62–0.63–0.64 (strong t, $CH_3(Si_n)$)
0.61 (weak shoulder, $CH_3(Si_2)$)
0.66 (weak shoulder, CH_2(a))
0.73 (weak shoulder, CH_2(b))
0.75 (br strong s, $CH_2(n)$)

routes are not stereoselective.[7] This fact was corroborated by the observed nonequivalences of the different methyl groups. In particular, the external methyl protons, $CH_3(Si_1)$, gave two singlets for all these short-chain models, while the internal methyl protons of **5**, $CH_3(Si_3)$, exhibited the aspect of a triplet resulting from isotactic and syndiotactic triad effects. As the same behavior was observed in the 200-MHz ^{1}H NMR spectrum of polycarbosilane **2**, one can conclude that this polymer too contained a mixture of stereosequences. Thus, the observed patterns result from stereosensitivity effects induced by asymmetric silicon atoms.

Complete ^{1}H NMR assignments for poly[(methylchlorosilylene)methylene] are given in Table III (see Figure 3). Integration and subsequent calculation of the intensity ratios yielded an average value of 21 for n in good agreement with the GPC curves.

Both ^{13}C and ^{29}Si NMR spectra of **2** exhibited three separate signals for each nucleus (as well as its CH_3 protons in the 200-MHz ^{1}H NMR spectrum), indicating that different configurational sequences must be taken into account. The ^{29}Si resonance peaks of **2**, centered at 25.70 and 28.35 ppm, were assigned to the internal and chain-end silicon nuclei, respectively, by comparison with the ^{29}Si chemical shifts of the carbosilane 3. Thus, it was concluded that the action of $Me_3SiCl/AlCl_3$ afforded a linear poly[(methylchlorosilylene)methylene] (2) with a linear structure:

$$CH_3\text{-}(SiCl(CH_3)CH_2)_{n'}\text{-}SiCl(CH_3)CH_3$$
$$\mathbf{2},\ \bar{n}' \simeq 23$$

Further NMR investigations of the polysilmethylene series are planned by the route of production of new short-chain models, in order to clarify the nature of the configurational sequences of this polymer.

Conclusion

Reaction of trimethylchlorosilane with poly[(dimethylsilylene)methylene] $-(Me_2SiCH_2)_n-$, in the presence of a catalytic amount of $AlCl_3$ led readily and quantitatively to a novel chlorinated polycarbosilane, $-(MeSiClCH_2)_n-$. It has been demonstrated that this polymer possesses a linear skeleton with $SiMe_2Cl$ groups at the chain-end terminals. Thanks to the versatile reactivity of its Si–Cl bonds, it opens the way to new polycarbosilane models with a clearly defined structure, useful in the fields of ceramic precursor studies and multinuclear NMR investigations.

Experimental Section

Starting Materials. Commercially available trimethylchlorosilane was distilled before use by distillation over magnesium turnings, under nitrogen in a column filled with glass helices. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane was synthesized according to Kriner's method.[9] It was a generous gift from Rhône-Poulenc Industries (bp_{760} = 119 °C).

Apparatus. All the reaction vessels were thoroughly dried and purged with dry nitrogen before use.

Characterization. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) with four Microstyragel columns calibrated by polystyrene standards (porosity ranges of 500, 10^3, 10^4, and 10^5 Å) and with THF as the eluent at a flow rate of 1 mL/min. The detection system used was a Waters Associates differential refractometer R 401.

Proton NMR spectra, 60 MHz, were checked on a Hitachi Perkin-Elmer R 24B spectrometer, in CCl_4 or $DCCl_3$ solutions (δ, ppm) and benzene as the internal standard.

Proton (200 MHz) and ^{29}Si NMR (39.76 MHz) spectra were checked with a Bruker AC 200 model, on polymer solutions in deuteriochloroform or benzene-d_6.

Infrared (IR) spectra were examined in the region 4000–600 cm^{-1} (neat product between NaCl plates).

Preparation of Poly[(dimethylsilylene)methylene] (1). Disilacyclobutane (100 g, 0.695 mol) was introduced in a 1-L flask fitted with a reflux condenser connected to a vacuum argon line. After introducing $H_2PtCl_6{\cdot}6H_2O$ (0.25 g), the reaction mixture was twice degassed by the freeze and thaw technique, evacuating to 0.1 mmHg. Finally the flask was allowed to warm to room temperature, in an argon atmosphere. The reaction flask then was lowered into an oil bath maintained at 80 °C. After 3 min, a violent polymerization accompanied by the evolution of white smoke occurred yielding a brown gum. Addition of 1.5 L of warm cyclohexane under magnetic stirring resulted within a few hours in the complete solubilization of the polymer. Filtration eliminated colloidal platinum and, after concentration on a rotary evaporator and devolatilization (0.5 mmHg at 100 °C), polymer **1** was obtained (96.5 g, 96.5%) as a brown rubber.

Preparation of 2. Polymer 1 (22.5 g, 0.313 mol of Si) and Me_3SiCl (170.9 g, 1.575 mol) were stirred under dry nitrogen in a 500-mL flask until complete dissolution. After addition of anhydrous $AlCl_3$ (1.25 g), the flask was set under a spinning band column equipped with a condenser in which ice water was circulated. The viscous brown solution was then warmed under magnetic stirring. When reflux temperature was reached, the mixture began to froth. After a few minutes, a notable fluidization was observed accompanied by an orange brown coloration, as well as the first drops of TMS condensing at the top of the column. The TMS was immediately distilled and 2 h later, more than half the theoretical quantity had been collected. The rate of TMS formation then slowly decreased and its separation became more difficult. After 8 h, the formation of TMS was complete (reflux temperature at the column top did not fall below 50 °C) and the mixture was left under argon. Thus, TMS (44 mL, theoretical value 42.6 mL) containing some Me_3SiCl fractions was collected by distillation: NMR titration allowed the root mean square quantity collected to be estimated as 97% of the theoretical value.

Filtration under nitrogen atmosphere followed by concentration with a rotary evaporator yielded a viscous liquid. Devolatilization under vacuum (1 mmHg) at 100 °C caused the elimination of any remaining Me_3SiCl and most of the aluminium chloride; 28.7 g of a fluid brown oil thus was obtained after cooling under argon. Assuming that the formulation is $-(MeClSiCH_2)_n-$, the reaction yield was estimated to be quantitative.

Elemental analysis based on **2**. Calcd: C, 26.28; H, 5.58; Cl, 38.03; Si, 30.13. Found: C, 25.78; H, 5.60; Cl, 37.20; Si, 29.60.

Acknowledgment. We are indebted to Rhône-Poulenc Industries for their generous gift of trimethylchlorosilane (chloromethyl)dimethylchlorosilane and 1,1,3,3-tetramethyl-1,3-disilacyclobutane. We are also grateful to Société Européenne de Propulsion (SEP) and Centre National de la Recherche Scientifique for their grant (E.B.).

Registry No. 1, 111113-80-5; 2 (SRU), 25722-25-2; 3, 31703-61-4; 1,1,3,3-tetramethyl-1,3-disilacyclobutane (homopolymer), 30029-85-7.

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New Polycarbosilane Models. 2. First Synthesis of Polysilapropylene

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ABSTRACT: Linear polycarbosilanes containing (methyl- and methyldeuteriosilylene)methylene units were synthesized for the first time and characterized by ^1H, ^{13}C, and ^{29}Si NMR. These polymers provide convenient models for studying both configurational sequence effects and Yajima's thermal polydimethylsilane–polycarbosilane rearrangement. Their terminal reticulation was investigated and the main gas evolved characterized.

Introduction

Yajima's route for the production of SiC requires the pyrolysis of polycarbosilanes (PCS) which are prepared by thermal rearrangement of poly(dimethylsilane) (PDMS), the latter resulting from the polycondensation of dimethyldichlorosilane.[1,2] This strategy is represented in Scheme I.

Scheme I

$$n(CH_3)_2SiCl_2 \xrightarrow[\text{2. methanol}]{\text{1. Na, toluene}} \underset{\text{PDMS}}{-(Si(CH_3)_2)_n-} \xrightarrow{470\ °C}$$

$$PCS \xrightarrow[N_2]{1200\ °C} SiC$$

This approach suffers from many limitations. For instance, the structures of the polymers (PDMS and PCS) remain poorly defined. The insolubility of PDMS hinders any detailed characterization of this material. In particular, the quantity and the structural influence of oxygen introduced by the methanolysis work-up is not readily measurable. In addition, the polycarbosilane structure is generally represented by the alteration of methylene and methylsilylene units, on the assumption that the thermal transformation proceeds according to Kumada's rearrangement.[3] This reaction was first observed with disilanes and formally amounts to the insertion of a methylene group into a Si–Si bond according to[3,4]

$$-Si(CH_3)_2Si(CH_3)_2- \xrightarrow{\Delta} -SiH(CH_3)CH_2Si(CH_3)_2$$

Unfortunately, the actual polycarbosilane cannot be accurately represented by the ideal structure $-(MeHSiCH_2)_n^-$. Beside the presence of Si–O bonds due to the PDMS oxygenation, Yajima[2] and other authors[5] have reported that PCS possesses a certain degree of cross-linking which cannot be taken into account by Kumada's transposition. Okamura[6] has even suggested the existence of cyclic patterns resulting from unknown secondary reactions leading to a complex framework for Yajima's PCS. Except these results, little information concerning the transformations polysilane–polycarbosilane and polycarbosilane–SiC can be found in the literature. In particular, for any given PCS precursor, the misunderstanding of its backbone structure rules out establishing any correlation between its structure, its thermal behavior, and its ability to yield a high SiC conversion rate. These questions prompted us to synthesize some polycarbosilane models of unambiguous formula, in order to examine their physicochemical properties and thermal behavior.

In our previous report,[7] we described the chemical modification of poly[(dimethylsilylene)methylene], leading to a poly[(chlorosilylene)methylene], as shown in Scheme II. The reduction of this polymer, yielding the corresponding poly[(methyl- and poly[(methyldeuteriosilylene)methylenes], is described in this paper.

Scheme II

$$\underset{1,\ \bar{M}_n\ 250\,000}{-(Si(CH_3)_2CH_2)_n-} \xrightarrow[AlCl_3]{(CH_3)_3SiCl}$$

$$\underset{2,\ \bar{M}_n\ 2300}{Cl(CH_3)_2SiCH_2-(SiCl(CH_3)CH_2)_{n'}-Si(CH_3)_2Cl}$$

Results and Discussion

Synthesis of the Polycarbosilanes. Lithium aluminum hydride reduction of Si–Cl bonds is usually carried out in solvents such as diethyl or dibutyl ether, THF, etc...[8] The corresponding silanes are obtained after treatment of the reaction mixture with dilute acid, which allows dissolution of the aluminum salts formed. This workup unfortunately entails hydrolysis of a few SiH bonds to give silanols or siloxanes, thus appreciably lowering the silane yields. Obviously, any aqueous treatment must be avoided to obtain a well-defined poly[(methylsilylene)methylene]. Some authors have overcome these problems by evaporating the ethereal solvent and replacement by hydrocarbons to precipitate the salts, the final product being recovered after filtration and distillation.

Models **3** and **4** were prepared in diethyl ether as the solvent (Scheme III), by modifying this latter procedure as reported later. Compound **3** can be regarded as an exact linear model of Yajima's theoretical polysilapropylene.

Scheme III

$$2 \xrightarrow[Et_2O]{LiAl\Sigma_4}$$

$$\underset{3,\ \Sigma = H;\ 4,\ \Sigma = D}{CH_3Si\Sigma(CH_3)CH_2-(Si\Sigma(CH_3)CH_2)_{n'}-Si\Sigma(CH_3)}$$

The chlorinated polycarbosilane **2** was readily converted into the corresponding hydrido or deuterio polymers after refluxing the reaction mixture for 24 h in an inert atmo-

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