

Formation of organosilicon compounds 115¹: the applicability as precursors for β -SiC of carbosilanes resulting from the gas phase pyrolysis of methylsilanes²

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Abstract

The thermal properties of polycarbosilanes from the gas phase pyrolysis of SiMe_4 , Me_3SiCl , Me_2SiCl_2 and the polymeric $(\text{Me}_2\text{Si}-\text{CH}_2)_n$ has been investigated. They decompose above 400 °C to form volatile methylsilanes, H_2 , CH_4 , viscous carbosilanes and insoluble glassy products via condensation reactions. The ceramic yield is between 10 and 20 wt.% at about 900 °C and falls to only a few weight per cent when heating is continued to 1000 °C. The gas phase pyrolysis of Me_2SiH_2 at 650 °C produces plastic, meltable polycarbosilanes (PCS). Tempering the compounds to 900 °C gives a ceramic residue in 85% yield with Si:C:H 1:1.2:0.4. Heating this residue under thermal gravimetry (TG) conditions to 1500 °C (argon atmosphere) results in a further weight loss of 0.7% and formation of β -SiC. Silicon carbide is also formed when the PCS from Me_2SiH_2 (Si:C:H 1:1.5:2.5) are heated to 1400 °C, with a weight loss of 16.3% under nitrogen and one of 42% in vacuum.

Keywords: Silicon; Pyrolysis; Carbosilanes; β -Silicon carbide

1. Introduction

We previously reported the formation and structures of low molecular weight carbosilanes produced by the gas phase pyrolysis of SiMe_4 and methylchlorosilanes at about 700 °C [2]. In their production, the evaporated methylsilanes together with the initially formed low molecular reaction products were circulated through the reaction zone. The high-boiling compounds were collected in cold traps under the reaction vessel. Reaction conditions, temperature and flow rate all influence the ratio of low to high molecular weight products, and longer reaction times lead to formation of a larger proportion of high molecular weight compounds. All the silanes $\text{R}_n\text{SiH}_{4-n}$ with $\text{R} = \text{Me}$ form molecular compounds with alternating Si and C atoms in the molecular framework, and the number of methyl groups in the starting compound determines the molecular structure of the carbosilanes formed.

The corresponding pyrolysis of EtSiCl_3 yields no carbosilanes but silicon compounds containing C–C double and triple bonds [3]. After the investigation and characterization of the low molecular weight carbosilanes, the next step was to investigate the products of higher molecularity and to study their applicability as precursors for silicon carbide. The following report deals with these investigations and related ones concerning the polymeric $(-\text{Me}_2\text{SiCH}_2-)_n$.

2. Results

2.1. The silicon-rich products of the pyrolysis of methylsilane

The yield of high molecular weight carbosilanes (oily and glassy solids) as products of pyrolysis decreases with the number of methyl groups in the starting methylsilane as follows: SiMe_4 47%, Me_3SiCl 40%, Me_2SiCl_2 30% and MeSiCl_3 2%.

The compounds SiMe_4 , Me_3SiCl and Me_3SiH form 1,3,5-trisilacyclohexanes and 1,3,5,7-tetrasiladaman-

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¹ Ref. [1].

² Dedicated to Professor Robert Corriu.

tan. In the case of Me_2SiCl_2 and MeSiCl_3 , besides 1,3,5-trisilacyclohexanes carbosilanes with barrelane and asterane frames are also formed. In order to obtain information about the mechanism of formation of the silicon-rich compounds we investigated the molecular composition of the compounds with five to ten Si atoms resulting from the pyrolysis of Me_3SiCl and Me_2SiCl_2 . This required separation by chromatographic methods, isolation of the compounds, and their characterization. Because SiCl -containing compounds are not suitable for HPLC, the relevant fractions were converted into the SiH derivatives with LiAlH_4 . To achieve separation we had to develop a special procedure involving consecutive steps. Separation depending on molecular weight (HPGPC), followed by separation depending on polarity (adsorption chromatography) and then by reverse phase chromatography allowed isolation of the compounds [4,5]. We isolated and characterized 41 compounds from the product mixture from the Me_2SiCl_2 pyrolysis and 25 compounds from the Me_3SiCl pyrolysis. The compounds formed from Me_2SiCl_2 contain, as a structurally defining group, the six-membered 1,3,5-trisilacyclohexane ring with C–Si–C–Si side chains and C or Si bridging (Fig. 1). Most of the compounds formed from Me_3SiCl contain the 1,3,5,7-tetrasiladamantane skeleton (Fig. 2). Compounds with C–C or Si–Si bonds are not observed. Details of the chromatographic separation and the characterization of the compounds (NMR, mass spectra) will be described elsewhere [6]. The results lead to the conclusion that the high molecular products from the pyrolysis of Me_2SiCl_2 and Me_3SiCl are oligomers whose structures are formed by condensation of the above-mentioned species (Figs. 1 and 2).

2.2. The thermal behaviour of polycarbosilanes from the gas phase pyrolysis of SiMe_4 , Me_3SiCl , Me_2SiCl_2 and $(-\text{Me}_2\text{Si}-\text{CH}_2-)_n$

In a study of the thermal behaviour of the polycarbosilanes, they were heated in an apparatus which allowed isolation of the gaseous, liquid and viscous compounds formed in cold traps for further investigation [4]. Starting from the temperature of initial decomposition, the compounds were heated in steps of 50 °C. The temperature was held constant at each step until no further increase of pressure could be detected.

The study also included the behaviour of polymeric $(-\text{Me}_2\text{Si}-\text{CH}_2-)_n$. From our work on the gas phase pyrolysis of SiMe_4 at 700 °C we know that $(\text{Me}_2\text{SiCH}_2)_2$ is formed and then immediately participates in the subsequent stages of the process [7]. We found that isolated $(\text{Me}_2\text{SiCH}_2)_2$ condenses at 300 °C to polymeric $(-\text{MeSi}-\text{CH}_2-)_n$ (a plastic elastic product) [8], whereas at 500 °C $(\text{Me}_2\text{SiCH}_2)_3$ and the Si-methylated 1,3,5,7-tetrasiladamantane are formed amongst other compounds [7]. (Other methods of forming $(-\text{Me}_2\text{Si}-\text{CH}_2-)_n$ are described in Ref. [8].)

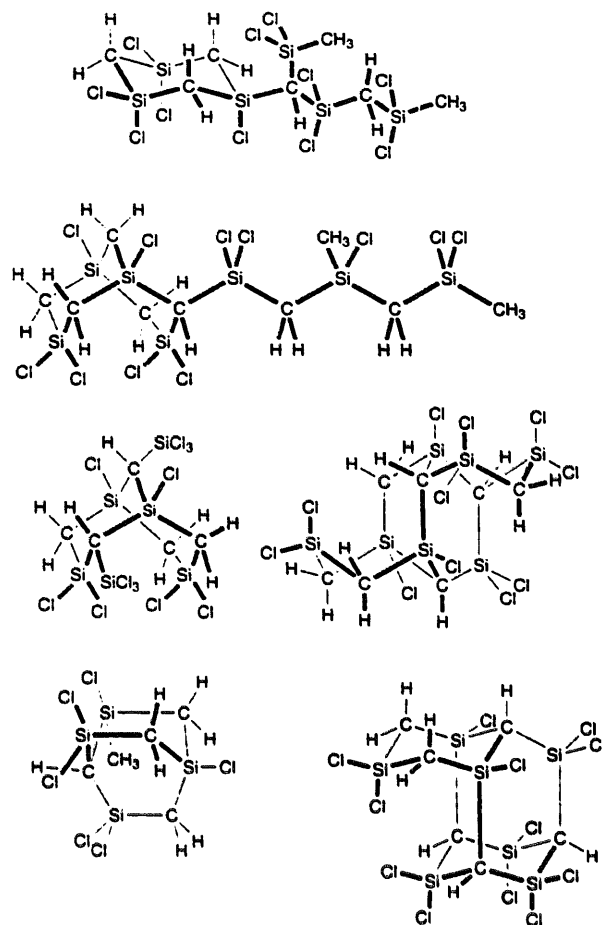


Fig. 1. Six characteristic carbosilanes (out of 41) from the gas phase pyrolysis of Me_2SiCl_2 at 700 °C containing four to seven silicon atoms in the molecule.

Table 1 contains the results of the thermolysis studies. The products of pyrolysis, which are solid at room temperature, melt between 200 and 300 °C. When the

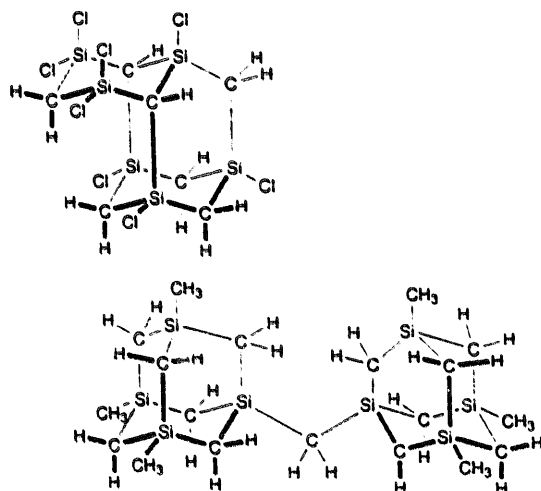


Fig. 2. Two characteristic carbosilanes (out of 25) from the gas phase pyrolysis of Me_3SiCl at 700 °C containing six to eight silicon atoms in the molecule.

Table 1

Results of the thermal treatment of polycarbosilanes (PCS) A from the gas phase pyrolysis of SiMe_4 , Me_3SiCl , Me_2SiCl_2 at 700°C and the polymeric $(-\text{Me}_2\text{Si}-\text{CH}_2-)_n$

A from	Products formed (amounts in mass% referred to A)								
	g	Si:C:H	°C	H ₂ /CH ₄ (ml g ⁻¹)	Methylsilane	Viscous distillate	Product		Si:C:H
							Insoluble	Soluble	
SiMe ₄	1:2.54:5.8								
	(a) 23.6		650	54.5	1.3	41	49		1:1.95:2.7
	(b) 20.4		400			32	^a 67	40	^a 1:2.52:5.4
	(c)* 5.6		500	7.3		14	84		
	(d)* 9.0		800	60.3			91		1:1.75:0.78
			1000 (TG)				10		
* (c) Reaction of product from (b); (d) reaction of product from (a)									
(-Me ₂ Si-CH ₂ -) _n	9.7		450					100	
	10.7		550	26.6	1.8	54		42	1:2.95:7.96
	6.2		600	146.6	6.5	54	18		
	7.2		800	191	4.2	61	19		1:1.74:0.63
			1000				9		1:1.7:0.7
Me ₃ SiCl	Si:C:Cl								
	1:1.8:0.92								
	(a) 14.9		650	25	6	57	35	10	
	(b) 32.5		430	3		27	73	100	
	(c) 20.4		530	12	3	47	^a 50	10	^a 1:1.8:0.75
	(d) 24.0		800	70	5	57	35		1:1.4:0.54
	(e) 17.9*		600	43	8	32	48		
	(f) 7.2*		700	62	7		89		1:1.5:0.61
^a (e) Reaction of product from (b); (f) reaction of product from (c)									
Me ₂ SiCl ₂	1:1.2:1.3								
	(a) 28		420	10	1.8	22.1		75.5	1:1.5:1.2
	(b) 12*		520	26	11.7	29.2	^a 55.8	^b 40	^b 1:1.9:1.0
									^a 1:1.6:0.9
	(c) 9.2		620	28	15.2	27.2	55.4	25	1:0.96:1.1
* (b) Reaction of product from (a)									

The IR spectra for PCS from TMS, Me_3SiCl_2 show the Si-H absorption band at 2100 cm^{-1} . In a qualitative view (no calibrated spectra) the amount of SiH in these compounds is considerably lower in comparison with the PCS from Me_2SiH_2 (Table 2).

mixture of compounds is heated above 300°C some of it becomes insoluble, and liquid and viscous products are formed which consist of low molecular weight carbosilanes such as 1,3,5-trisilacyclohexane and 1,3,5,7-tetrasiladamantane respectively, already known

from gas phase pyrolysis. The residue which remains when the substance is heated to 800°C has a lower C-content than the initial starting material. There is a remarkably large amount of a mixture of viscous carbosilanes that distills at above 400°C . This was also

Table 2

Results of the thermal treatment of polycarbosilanes (PCS) B from the gas phase pyrolysis of Me_3SiH , Me_2SiH_2 and $(-\text{MeHSi}-\text{CH}_2-)_n$

B from	Products (amounts in mass% referred to B)								
	g	Si: C: H	°C	H ₂ /CH ₄ (ml g ⁻¹)	Methylsilane	Viscous distillate	Product		Si: C
							Insoluble	Soluble	
Me ₃ SiH	4.92	40% Si	200					melt	
			350		1				
			800		28	10.4	52.6		1: 1.4
Me ₂ SiH ₂	2.94	1: 1.5: 2.5 *	650						
			900				85.3		1: 1.2: 0.4

* The IR spectrum (KBr Pellet) shows the following absorption bands (cm^{-1}): C-H 2943.2; Si-H 2095.9; $-\text{CH}_2-$ 1404.5 and 1354.3; Si- CH_3 1248.2, $-\text{CH}_2-$ 1017.2; Si-H 833.3. The PCS is an amorphous pale yellow product which becomes viscous above 140°C and forms a pale yellow melt at 165°C . From this melt it should be possible to pull out fibres. Further investigations are underway.

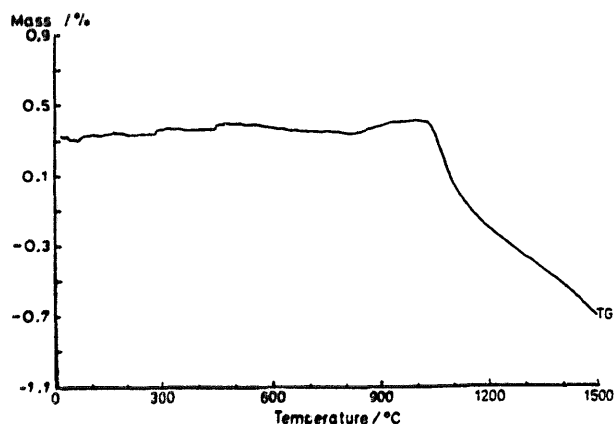


Fig. 3. TG diagram of the PCS from Me_2SiH_2 tempered at 900 °C (Table 2 with Si:C:H 1:1.5:2.5) in argon atmosphere.

observed in the case of the products from Me_3SiCl and Me_2SiCl_2 pyrolysis, and indicates the complexity of the decomposition and condensation reactions. Further heating of the compounds (TG) to 1500 °C results in a fall of the ceramic yield to only a few per cent, and so it can be concluded that the polycarbosilanes synthesized in this way are not suitable precursors for β -SiC.

2.3. Thermal behaviour of polycarbosilanes from the gas phase pyrolysis of Me_3SiH and Me_2SiH_2

Investigations of the thermal behaviour of Si-H-containing polycarbosilanes resulting from gas phase pyrolysis of Me_3SiH and Me_2SiH_2 were carried out to allow comparisons with those obtained from SiMe_4 , $(-\text{SiMe}_2-\text{CH}_2-)_n$, Me_3SiCl and Me_2SiCl_2 . The results of these investigations are shown in Table 2.

For the further thermal gravimetric investigations we used:

(a) PCS B from Me_2SiH_2 pyrolysis tempered at 900 °C to give a composition Si:C:H 1:1.2:0.3 (Table 2);

(b) PCS B from Me_2SiH_2 pyrolysis (without thermal pretreatment) having the composition Si:C:H 1:1.5:2.5 (Table 2).

Fig. 3 shows the TG curve of the tempered carbosilane (a) in the region from 20 to 1500 °C. The weight loss is 0.7%. The X-ray powder pattern of the residue shows the presence of β -SiC (Fig. 4).

The TG diagram in Fig. 5 shows the thermal behaviour of the PCS from Me_2SiH_2 (b) in the range 20 to 1400 °C. In a nitrogen atmosphere (flow rate 50 ml h^{-1}) the weight loss is 16.3% and in vacuum it is 42%. Fig. 6 shows the influence of the heating rate on the reaction rate: (a) 3 °C min^{-1} , (b) 8 °C min^{-1} . The higher heating rate in (b) results in a faster weight loss and curve (b) crosses curve (a) at 200 °C. In both cases (nitrogen atmosphere and vacuum) the X-ray powder pattern, like that in Fig. 4, shows the formation of β -SiC.

3. Discussion

A recent review by Dunogues and coworkers [9] reports the current state of investigations of the formation and applicability of polymeric precursors for the production of β -SiC. Our special procedure for gas phase pyrolysis of methylsilanes at about 700 °C permits formation of high molecular weight polycarbosilanes (exclusively with alternating Si and C atoms in the molecular framework) by reactions of the methylsilanes

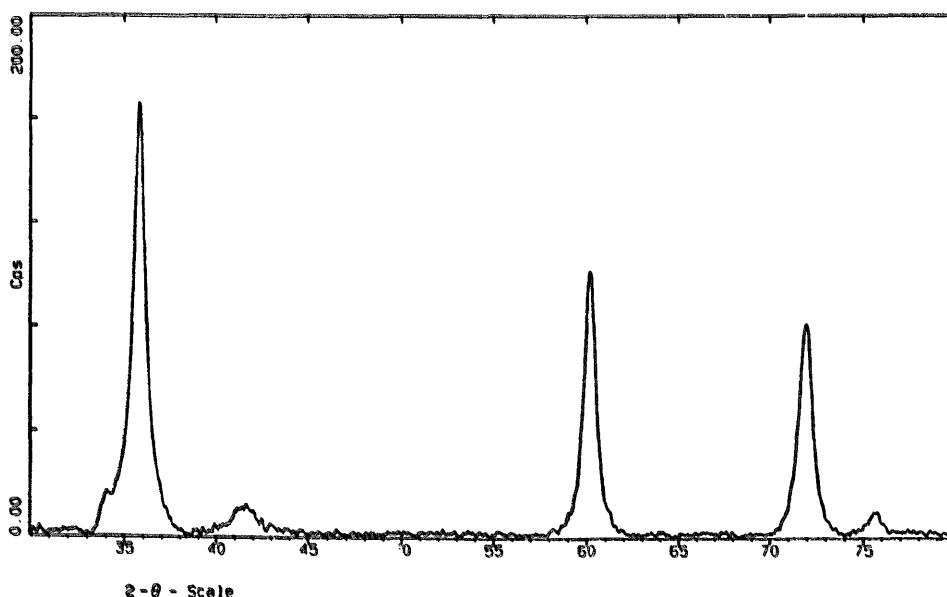


Fig. 4. X-ray powder pattern from the residue formed from the TG experiment shown in Fig. 3.

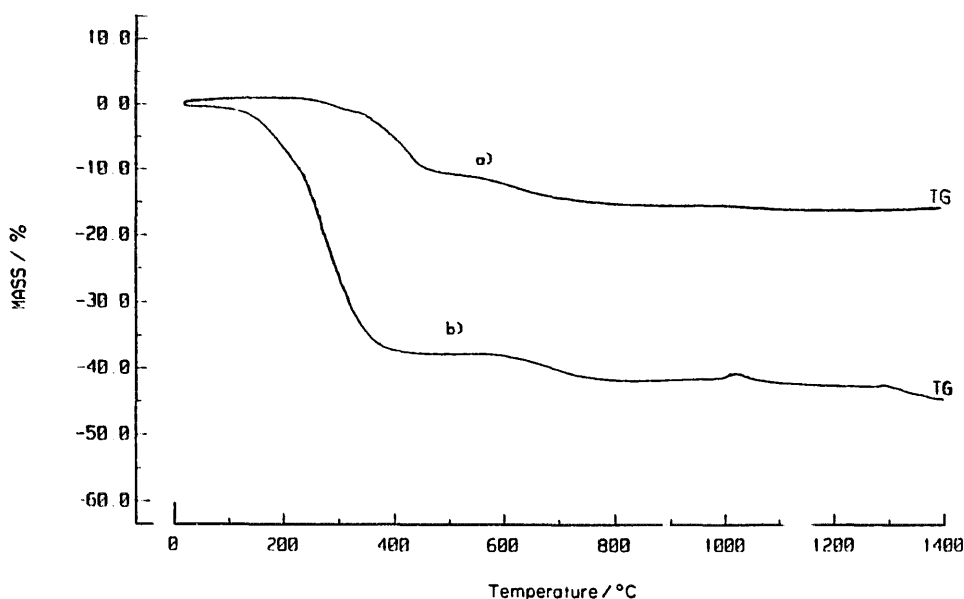


Fig. 5. TG diagram of the PCS from Me_2SiH_2 not tempered (Table 2 with Si:C:H 1:1.5:2.5) in nitrogen atmosphere (weight loss 16.3%) and vacuum (weight loss 42%).

with the already formed low molecular weight carbosilanes on the one hand, and with themselves on the other. The products are viscous, glassy meltable, and partly insoluble solid compounds. From knowledge of the structures and compositions of the low molecular weight products of pyrolysis, with a molecular weight of up to 400 (for halogen-free compounds) (Figs. 1 and 2), it can be assumed that the high molecular weight carbosilanes are formed by condensation via Si–C links of these cyclic and oligocyclic compounds. The results

presented in Table 1 for the thermal treatment of the PCS formed from SiMe_4 , Me_3SiCl and Me_2SiCl_2 show that these polymers are further modified above 400 °C. Results obtained by Yajima and coworkers [10] in analogous investigations on polydimethylsilanes and polycarbosilanes from the gas phase pyrolysis of SiMe_4 , PCS-TMS, (TG investigations) are in agreement with those presented in Table 1.

Our investigations, which gave the results in Table 1, show that the condensation reactions upon heating of

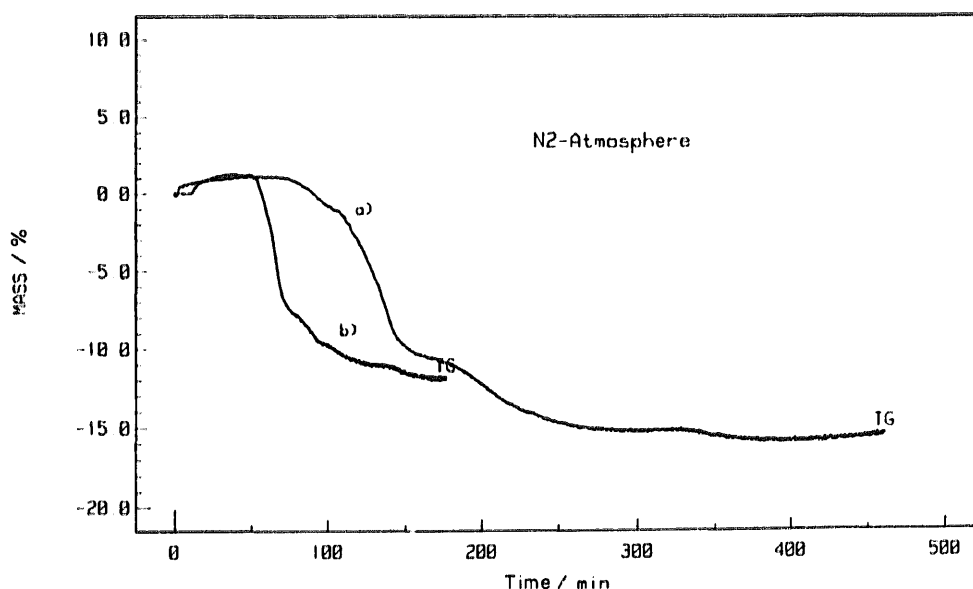


Fig. 6. TC diagram of the PCS from Me_2SiH_2 not tempered (Table 2 with Si:C:H 1:1.5:2.5) in a nitrogen atmosphere with different heating rates: (a) $3\text{ }^\circ\text{C min}^{-1}$, (b) $8\text{ }^\circ\text{C min}^{-1}$.

PCS-TMS result not only in elimination of H_2 , CH_4 and low molecular weight methylsilanes, but also in viscous carbosilanes as a distillate. The ceramic yield, however, decreases between 1000 and 1500 °C to a low value. This is exactly the same as with $(-\text{Me}_2\text{SiCH}_2-)_n$ and the PCS formed from Me_3SiCl and Me_2SiCl_2 . Therefore, the polycarbosilanes formed are not suitable precursors for the formation of β -SiC, although the C:Si ratio in the product falls at higher temperatures. The PCS from the gas phase pyrolysis of Me_3SiH and Me_2SiH_2 gave much better results. The ceramic yield from the PCS B from Me_2SiH_2 , with Si:C:H 1:1.2:0.3, which are obtained at 900 °C is clearly better than those from the PCS A (Table 1). It is informative to compare the ratio Si:C:H in the PCS from SiMe_4 (Si:C:H 1:2.54:5.8) with that obtained from Me_3SiH (1 2.3:5.6) and the ceramic yields of these materials at 800 °C. The ceramic yield of the PCS from SiMe_4 decreases to 10% and that of the PCS from Me_3SiH to 47%. When PCS from SiMe_4 is heated, 90% of a viscous carbosilane mixture distills out between 650 and 800 °C. In contrast, only 10% distills out as a viscous product from the PCS obtained from Me_3SiH . The ceramic yields from polymeric $(-\text{Me}_2\text{Si}-\text{CH}_2-)_n$ and from the PCS obtained from SiMe_4 at 800 °C are both 10%, although the structures of the products are different. We thus conclude that the structural difference has no influence on the ceramic yield. Compared with the behaviour of the polycarbosilanes listed in Table 1, the presence of Si-H bonds in the PCS from Me_3SiH , Me_2SiH_2 (and MeSiH_3 [11]) improves the condensation to the ceramic product. This agrees with the results of investigations on $[-\text{H}_2\text{Si}-\text{CH}_2-]_n$ by Smith [12] and Interrante and coworkers [13].

The TG investigations and X-ray powder patterns (Figs. 3, 4, 5 and 6) show that β -SiC is formed from the PCS from Me_2SiH_2 (Table 2). The weight loss in the measurements under either an argon or a nitrogen atmosphere is about 16 to 17%, and in vacuum about 42%.

An advantage of the PCS from Me_2SiH_2 when compared with those described in Refs. [12,13] is that Me_2SiH_2 can easily be made from Me_2SiCl_2 and that the gas phase pyrolysis yields the polycarbosilanes without significant problems.

4. Experimental

4.1. Instrumental

Thermal gravimetric measurements were carried out with a Co. Netzsch STA 409 apparatus, Pt/Rh furnace, TG-DTA sample holder in Al_2O_3 crucibles. The IR spectrum was recorded with KBr pellets on an FT-IR spectrometer (Bruker IFS 28). X-ray powder patterns were obtained with a Stoe Stadi P, Cu $\text{K}\alpha$, 35 mA 40 kV instrument.

4.2. Thermal gravimetric experiments

Fig. 3: initial weight 156.86 mg, Ar atmosphere, heating rate 5 °C min^{-1} , weight loss 0.7%.

Fig. 5: (a) initial weight 43.0 mg, N_2 atmosphere, heating rate 3 °C min^{-1} , weight loss 16.3%; (b) initial weight 30.9 mg, 5.9×10^{-4} mbar, heating rate 3 °C min^{-1} , weight loss 42.0%.

Fig. 6: (a) initial weight 43.0 mg, N_2 atmosphere, heating rate 3 °C min^{-1} , weight loss 16.3%; (b) initial weight 50.5 mg, N_2 atmosphere, heating rate 8 °C min^{-1} , weight loss 13.0%.

4.3. Synthesis of Me_2SiH_2

Me_2SiH_2 was made by reaction of Me_2SiCl_2 with LiH in an LiCl/KCl salt melt at 400 °C [14]. Before the LiH was added the salt melt was heated in vacuum to 400 °C in order to remove water. Then Me_2SiCl_2 was heated to its boiling point and bubbled through the melt with He as carrier gas. The hydrogenation proceeded steadily and was complete with respect to both Cl atoms, giving Me_2SiH_2 in a yield of above 90%. The Me_2SiH_2 was condensed in cold traps and purified from traces of Me_2SiCl_2 (^1H , ^{29}Si NMR spectra) by fractional condensation.

4.4. The products of Me_2SiH_2 pyrolysis

The pyrolysis of Me_2SiH_2 was carried out at 620 °C with 500 g of Me_2SiH_2 (for further details see Ref. [2]), and 455 g (91%) of high molecular weight compounds with a boiling point above 60 °C were isolated. From the reactor tube we isolated 71 g of a residue which is insoluble in organic solvents and has not yet been investigated further. In the traps under the reactor tube we collected 384 g of a fluid mixture of high molecular weight compounds. These were separated by distillation at 190 °C and 0.01×10^{-3} Torr to yield 95 g of a pale yellow powder (PCS from Me_2SiH_2 , Table 2) and 295 g of a fluid mixture of carbosilanes. The pale yellow powdery PCS forms a viscous melt between 140 and 160 °C. The gaseous and high volatile compounds formed in pyrolysis are similar to those from earlier investigations of Me_2SiH_2 pyrolysis [2].

Acknowledgements

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