Review

Poly(silylenemethylenes) — a novel class of organosilicon polymers [1]

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Abstract

The synthesis and investigation of the poly(silylenemethylene)s, linear polymers with a regular $-RR'SiCH_2-$ repeat unit, are reviewed, particularly from the standpoint of recent work carried out in the authors' own laboratory in the past few years. Improvement in the synthetic routes to the substituted disilacyclobutanes used as monomers in the ring-opening polymerization process employed for the synthesis of these polymers has enabled the preparation of a wide range of new polymers of this type. This range of polymers has been extended further by using reactive functionalities on Si in polymers containing Si-Cl, Si-OR and Si-H groups to append various side chains on to the polymer backbone. The parent polymer in this series, polysilaethylene, has been studied as an analog of polyethylene and as a precursor for silicon carbide, leading to information about the crystalline structure for the solid form of this polymer, as well as on the polymer-to-ceramic conversion process. The ethoxy-substituted polymer, $[Si(OEt)_2CH_2]_n$, undergoes hydrolysis and condensation on treatment with water to produce a gel which has an inorganic (Si–O–Si)/organic (Si–CH$_2$–Si) network structure. Upon pyrolysis to 1000°C, this gel is converted into a silicon oxycarbide having a full distribution of $SiC_{4-x}O_x$ ($x = 0-4$) microenvironments.

Keywords: Silicon carbide; Poly(silylenemethylenes); Ceramic precursors; Silicon oxycarbide

1. Introduction

The poly(silylenemethylenes) (PSMs), $[RR'SiCH_2]_n$, constitute a relatively neglected class of organosilicon polymers that are beginning to receive increasing attention as both ceramic precursors and as novel polymeric materials. The first PSMs were reported in 1949–50 as low molecular weight products of the coupling of chlorocarbosilanes by using active metals [1]. It was later found that much higher molecular weight polymers could be obtained from the ring-opening polymerization (ROP) of disilacyclobutanes (DSCBs) by using heat or various late transition metal catalysts, among which platinum compounds seemed to be the most effective [2]. However, the early work in this area was largely limited to polymers with methyl or phenyl groups on silicon and was hindered by the lack of suitable high-yield routes to the DSCB monomers. Attempts to introduce a reactive group on silicon by the polymerization of a chloro- or ethoxy-substituted monomer [2d] or by

functionalizing poly(dimethylsilylene)methylene [3] resulted in low molecular weight products. The discovery in our laboratory that the polymerization and subsequent reduction of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane and 1,1,3,3-tetrachloro-1,3-disilacyclobutane resulted in high molecular weight polysilapropylene (1) [4] and polysilaethylene (2) [5] respectively, effectively opened up some new routes to a wide range of PSMs. In these cases, there is both the Si–Cl functionality of the chloropolymer intermediates and the Si–H bond in the corresponding reduced polymers as potential reactive sites for chemical substitution on Si. We describe below the preliminary results of our efforts to exploit this approach to prepare a wide variety of substituted PSMs. In addition to substitution reactions on preformed Si–Cl and Si–H-substituted polymers, we have also explored the direct synthesis of PSMs by ROP of the corresponding DSCB monomers. In this case, as in the previous one, a major limitation in the ability to prepare new polymers has been the availability of convenient, high yield routes to the corresponding DSCB monomers. Our efforts to overcome this key problem, as well as to prepare new PSMs by using these monomers, are described in this review. Finally, we report the results of our studies of some of these

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[1] Dedicated to Professor Robert Corriu in recognition of his many contributions to organosilicon chemistry.

polymers as precursors to ceramic materials, such as SiC and SiO_xC_y.

## 2. Synthesis and investigation of new silylenemethylene monomers and polymers

2.1. Development of improved syntheses for the DSCB monomers

Unlike their all-carbon analogs, the polyolefins, where the corresponding olefins are generally available for use as monomers, in the case of the PSMs the most effective way to make high molecular weight linear polymers is by means of ROP of 1,3-DSCB monomers [2]. In 1964, Kriner developed the so-called 'reverse addition' procedure to prepare DSCB derivatives [6]. This approach involves the slow addition of Mg powder to a solution of the chlorocarbosilane starting material (typically, $ClRR'SiCH_2Cl$) and results in an improved yield of the four-membered ring product over higher oligomers and polymer relative to the usual method of adding the chlorosilane to the Mg. It is particularly suitable for disubstituted alkyl and aromatic chlorocarbosilanes (i.e. $ClRR'SiCH_2Cl$, where R and R' = alkyl or aryl) and has recently been employed to prepare various alkyl- and aryl-substituted 1,3-DSCBs [7,8]. For the preparation of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane, Kriner employed a three-step reaction procedure, starting with the ethoxy-substituted compound, $Cl(EtO)Si(Me)CH_2Cl$, in a 'reverse addition' Grignard reaction (Scheme 1). This provides a reasonable yield (ca. 30%) of the corresponding four-membered ring product, whereas the alternative $Cl_2(Me)SiCH_2Cl$ yields a mixture of oligomeric products and polymer that contains little or no 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane. The 1,3-diethoxy-1,3-dimethyl-1,3-disilacyclobutane can then be con-
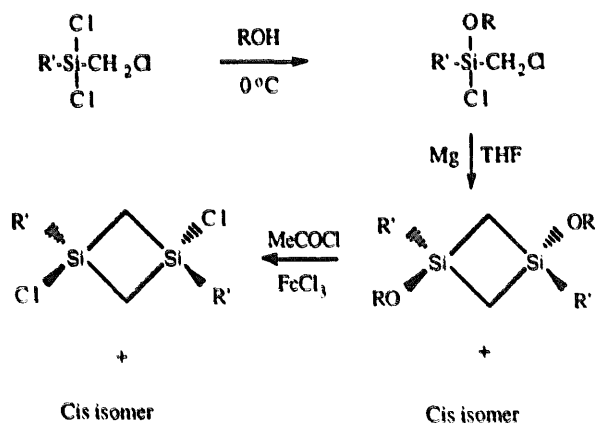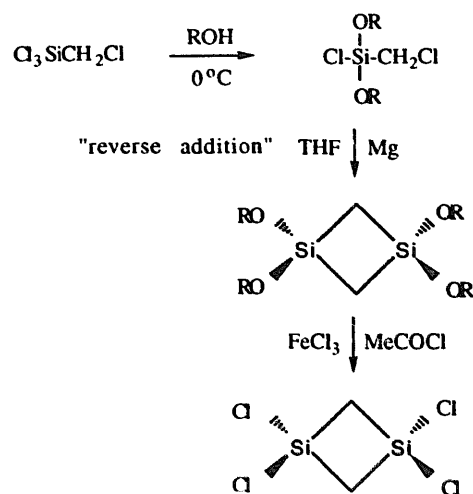

Scheme 2. Synthetic route for TCDSCB.

verted into the 1,3-dichloro-1,3-dimethyl-product by using benzoyl chloride plus $FeCl_3$ [6].

The role of the ethoxy group in improving the yield of the four-membered ring product in this case is presumably based on a combination of the reduced reactivity of the ethoxysilane compared with that of the chlorosilane in Grignard coupling reactions, as well as to its greater steric effect which limits the extent of oligomerization at the expense of ring closure of the initially formed dimeric species, $Cl(OEt)(Me)SiCH_2Si-(OEt)(Me)SiCH_2Cl$. In order to investigate the effect of the size of the alkyl group on this oligomerization process, we examined the series of alkoxycarbosilanes $(Cl(OR)(Me)SiCH_2Cl$, where R = Me, Et and ^iPr [9]) as substrates for the 'reverse addition' Grignard coupling reaction. It was found that the iso-propoxy compound gave the highest yield of the 1,3-DSCB product, the 50% yield being a substantial improvement over the 35.3% for the ethoxy substituent originally used by Kriner [2d]. This improved yield was presumably due to steric effects which inhibit further oligomerization during the 'reverse addition' Grignard reaction. Moreover, we found [9] that 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane could be obtained in a much improved yield from 1,3-dimethyl-1,3-diisopropoxy-1,3-disilacyclobutane by using acetyl chloride rather than benzoyl chloride [6], as the chlorinating reagent. Separation of the products by distillation was simplified due to the lower boiling points of the by-product (isopropyl acetate) and the residual starting material (acetyl chloride). The overall yield in the current three-step synthesis is 32%, which is considerably higher than that previously reported (15.6%) [2d].

As shown in Scheme 2, 1,1,3,3-tetrachloro-1,3-disilacyclobutane (TCDSCB) was prepared similarly to the dimethyldichloro-derivative, starting from chloromethyltrichlorosilane. In this case, the diethoxy-substituted compound $Cl(EtO)_2SiCH_2Cl$ gave the highest yield

R = i-Pr; R' = Me, Ph, and n-Hex

Scheme 1. Synthesis of 1,3-dichloro-1,3-disilacyclobutanes.
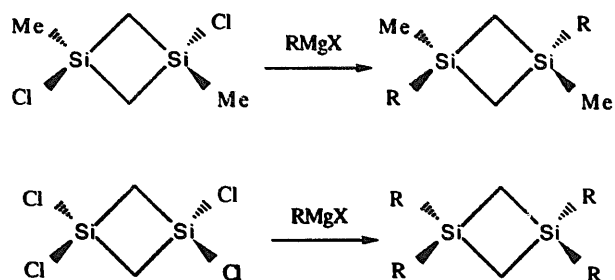
Scheme 3. Synthesis of 1,3-dialkyl-1,3-dimethyl-1,3-disilacyclobutanes and 1,1,3,3-tetraalkyl-1,3-disilacyclobutanes.

(40%) in the ring closure Grignard reactions [9]. In addition, we also found that the six-membered ring species 1,1,3,3,5,5-hexamethoxy-1,3,5-trisilacyclohexane could be obtained in 50% yield via a 'reverse addition' Grignard coupling of $(MeO)_3SiCH_2Cl$. The ethoxy-substituted four-membered ring and the methoxy-substituted six-membered ring species can also be converted into the corresponding chlorinated products in high yield by using acetyl chloride. Moreover, the resultant chloro-substituted cyclic carbosilanes can be reduced with $LiAlH_4$ to yield the corresponding parent DSCB and trisilacyclohexane in higher yields than in the previously described preparations of these compounds.

With the availability of improved methods for the synthesis of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane and tetrachloro-1,3-disilacyclobutane, these compounds can be employed as the starting materials for the synthesis of a large number of substituted 1,3-DSCBs (Scheme 3) by Grignard coupling reactions. The alkyl groups in both the dimethyldialkyl- and tetraalkyl-1,3-disilacyclobutanes prepared ranged from ethyl to n-hexyl. The yields of the Grignard coupling reactions between the RMgX reagents and these two chloro-substituted cyclic carbosilanes vary from 70 to 90%. In general, the short chain alkyl species were obtained in higher yields. Owing to the improved availability of the cyclic chlorocarbosilanes, along with typically low yields (30%) exhibited by the Cl_3SiCH_2Cl plus RMgX reaction [8], this procedure provides the best route to these alkyl-substituted 1,3-DSCBs.

Monomers leading to PSMs containing -SiHR'- linkages, where R' is an alkyl or aryl group other than methyl, such as phenyl or n-hexyl, are also conveniently prepared by the route shown in Scheme 1. The R'-substituted starting material, $Cl_2(R')SiCH_2Cl$, for these reactions can be obtained from the Grignard coupling of Cl_3SiCH_2Cl with R'MgCl.

2.2. Synthesis and characterization of poly(1-silaethylene) (PSE)

We had previously shown that ROP of TCDSCB, followed by reduction with $LiAlH_4$, yields a high molecular weight (M_w = ca. 80000 AMU) form of PSE (2), $[SiH_2CH_2]_n$, the monosilicon analog of polyethylene (PE) [5]. The TCDSCB used in this earlier work was obtained from 1,1-dichloro-1-silacyclobutane $[-SiCl_2(CH_2)_2CH_2-]$ by high temperature pyrolysis. The new procedure described herein provides the TCDSCB monomer in much higher yield from a much less expensive starting material. Moreover, it is much more convenient to carry out on a large scale in the laboratory. This has allowed us to prepare significant quantities of PSE for detailed studies of its molecular structure and phase transitions. Recently completed solution ^1H, ^{13}C, and ^{29}Si NMR studies indicate that this polymer contains CH_3 and SiH_3 end groups and a very small amount SiH branch sites due to the presence of methyl side groups [10]. Moreover, we were able to identify the source of these methyl groups which, in a typical preparation, amount to ca. 1/200 Si atoms, as a small amount of the corresponding methyltrichlorodisilacyclobutane formed from some Me_2SiCl_2 in the original $MeSiCl_3$ starting material used for this synthesis.

We have also found that this monosilicon analog of PE, PSE, possesses interesting similarities, and differences, in physical properties with respect to PE [11]. In particular, like PE, PSE forms a highly crystalline solid; however its T_m is much lower than that of PE, presumably due to the large configurational entropy that results from the high mobility of the PSE chains. This high chain mobility was evidenced by solid state NMR measurements, which provided a value for the chain torsional barrier substantially lower than that previously observed for PE but quite close to that predicted by theoretical studies of a small molecule analog, 1,3,5-trisila-n-pentane. The origin of this low barrier for chain torsion arises from the lower H-H repulsive interactions encountered on rotation about the relatively longer Si-C intrachain bonds in PSE, compared with those for rotation about the C-C backbone bonds in PE. The initial indications, from solid state ^{13}C NMR spectroscopy, of an all-trans conformation for the PE chains in the crystalline form have been recently confirmed by wide-angle X-ray diffraction (XRD) and IR-Raman studies carried out on PSE and its $[SiD_2CH_2]_n$ isotopomer in conjunction with detailed ab initio calculations on small molecule analogs [12]. The results of these studies have not only demonstrated the existence of an all-trans conformation for the PSE chain analogous to that found for PE, but have also provided unit cell dimensions for the PSE structure which, of course, differ significantly from those for PE.

## 2.3. Preparation of alkyl- and phenyl-substituted PSMs

As indicated in Schemes 4 and 5, ROP of the substituted 1,3-DSCBs can be initiated by adding chloropla-
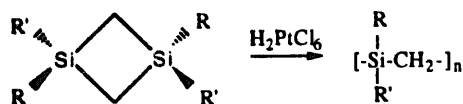
Scheme 4. Synthesis of the [SiRR'CH$_2$]$_n$ polymers.

tinic acid to the neat liquids, except for 1,3-dichloro-1,3-diphenyl-1,3-disilacyclobutane, which was polymerized in solution because it is solid, and sublimes very easily when heated. The chloro-polymers can be reduced by LiAlH$_4$ to yield the corresponding hydrides [13]. The weight average molecular weights, measured by GPC, of the obtained polymers ranged from 11 000–460 000 AMU, with a relatively narrow polydispersity (typically around 2–3).

It was found that all of the dialkyldimethyl-DSCB monomers could be polymerized to form high molecular weight ($M_w > 70000$ AMU) polymers under conditions similar to those used for 1,1,3,3-tetramethyl-1,3-disilacyclobutane [2]. The ROP of the tetraalkyl-DSCB monomers gave the symmetrically substituted dialkyl polymers, [SiR$_2$CH$_2$]$_n$. In contrast to the asymmetrically substituted polymers, [SiMe(R)CH$_2$]$_n$, the molecular weights of the [SiR$_2$CH$_2$]$_n$ polymers decreased with an increase of the length of the alkyl groups ($M_w =$ 55 000 → 15 000; R = Et → n-Hex), presumably owing to steric hindrance from the alkyl groups during the ROP.

As expected from the non-sterospecific nature of the polymerization process, as well as from the fact that the starting DSCBs were all obtained as cis–trans mixtures from the above preparation procedures, the corresponding asymmetrically substituted polymers, [SiMe(R)CH$_2$]$_n$ (R = Et, n-Pr, n-Bu, n-Pe, n-Hex, and Ph) and [SiH(R)CH$_2$]$_n$ (R = n-Hex and Ph), were found by NMR spectroscopy to adopt an atactic configuration. The glass transition temperatures T_gs determined for these asymmetrically substituted PSMs are listed in Table 1. For the polymers with relatively long and flexible R groups, such as n-hexyl, lower T_gs were observed; the polymers with rigid side groups, such as phenyl, showed higher T_gs. Some of these [SiMe(R)CH$_2$]$_n$ and [SiH(R)CH$_2$]$_n$ polymers can be regarded as the monosilicon analogs of well-known [CMe(R)CH$_2$]$_n$ and [CH(R)CH$_2$]$_n$ polymers. The T_g values for these C–C

R'= R = Me, n-Hex, and Ph
or R = Cl, R' = H
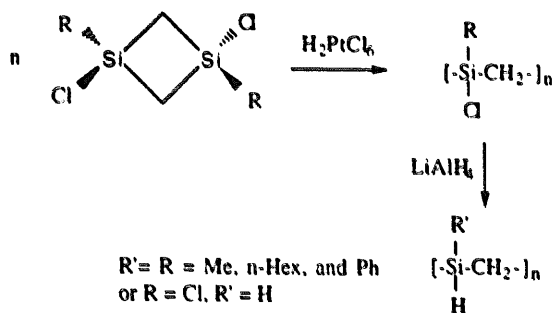
Scheme 5. Synthesis of the [SiH(R)CH$_2$]$_n$ polymers.

Table 1
Glass transition temperatures for [SiRR'CH$_2$]$_n$ polymers

Polymer	T_g(°C)
[SiMe(Et)CH$_2$]$_n$	−78.2
[SiMe(n-Pr)CH$_2$]$_n$	−61.2
[SiMe(n-Bu)CH$_2$]$_n$	−63.0
[SiMe(n-Pe)CH$_2$]$_n$	−64.9
[SiMe(n-Hex)CH$_2$]$_n$	−71.1
[SiH(n-Hex)CH$_2$]$_n$	−91.4
[SiMe(Ph)CH$_2$]$_n$	+28.6
[SiH(Ph)CH$_2$]$_n$	−37.6

Table 2
Comparison of T_gs for the [SiRR'CH$_2$]$_n$ and [CRR'CH$_2$]$_n$ polymers

Polymer	[CMe(Ph)CH$_2$]$_n$	[SiMe(Ph)CH$_2$]$_n$
T_g (°C)	168	28.6
Polymer	[CH(Ph)CH$_2$]$_n$	[SiH(Ph)CH$_2$]$_n$
T_g (°C)	100	−37.6
Polymer	[CH(n-Hex)CH$_2$]$_n$	[SiH(n-Hex)CH$_2$]$_n$
T_g (°C)	−65	−91.4

backbone polymers [14] and their Si–C analogs are compared in Table 2. As was observed for the T_m value for PSE vs. that for PE, the glass transition temperatures of the [SiR'(R)CH$_2$]$_n$ polymers are all lower than those of the corresponding carbon-backbone polymers, [CR'(R)CH$_2$]$_n$. Again, this presumably reflects the higher chain flexibility of the PSMs relative to the polyolefins due to the greater length of the Si–C backbone bonds [11,12].

As was reported recently for the di-propyl derivative [8], the dialkyl-substituted polymers [SiR$_2$CH$_2$]$_n$ all showed two endothermic transitions in the differential scanning calorimetry (DSC), with the final transition leading to an isotropic melt, as evidenced by optical microscopy [9]. In these cases, the low temperature solid forms of the polymers are crystalline, as suggested by both optical microscopy and wide-angle XRD. The respective transition temperatures are summarized in Table 3. Following the assignment of the somewhat analogous transitions previously observed for the corresponding poly(di-n-alkylsiloxanes) [15] and poly(di-n-alkylsilanes) [16], the first transition might be assigned as a solid disordering transition or a solid–solid structural transformation and the second one as an isotropic melting transition. However, the intermediate phases in

Table 3
Transition temperatures for the [SiR$_2$CH$_2$]$_n$ polymers

Polymers	T_1 (°C)	T_2 (°C)
[SiEt$_2$CH$_2$]$_n$	58	70
[Si(n-Pr)$_2$CH$_2$]$_n$	79	86
[Si(n-Bu)$_2$CH$_2$]$_n$	81	96
[Si(n-Pe)$_2$CH$_2$]$_n$	55	65
[Si(n-Hex)$_2$CH$_2$]$_n$	50	55

T_1: first transition; T_2: second transition.

these PSMs apparently exist in a very narrow temperature range compared with those phases in the poly(siloxanes) $[SiR_2O]_n$ and poly(silanes) $[SiR_2]_n$, and this makes their detailed study more difficult.

We also investigated the thermal stability of these PSMs [13]. Under nitrogen, the alkyl-substituted polymers decompose near 400°C and give very low ceramic yields when heated to 1000°C. Polymers containing Si–H groups were found to decompose at lower temperature, but give higher ceramic yields, presumably because of crosslinking induced by the loss of hydrogen from the Si–H groups (see section on ceramic precursors below) [17].

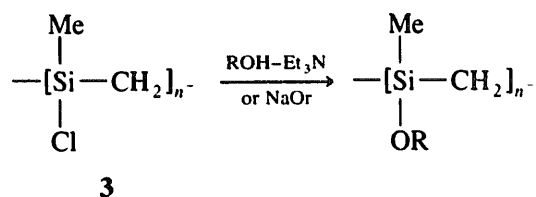## 2.4. Preparation of dialkoxy-substituted PSMs

Extensive research has been carried out on the structural and thermal properties of the poly(dialkoxyphosphazenes), especially poly[bis(trifluoroethoxy)phosphazene] [18]. The latter polymer has found application as an advanced elastomer in the aerospace and automobile industries [18]. Unlike the polysiloxanes for which dialkoxy-substituted polymers are not synthetically accessible, we have found that the PSMs can potentially afford a wide range of dialkoxy-substituted polymers that combine the good hydrolytic stability of the Si–C backbone with the synthetic flexibility of the polyphosphazenes. Our initial efforts in this area [19] have focused on the synthesis of the diethoxy- and bis(trifluoroethoxy)-PSMs in order to allow a direct comparison with the corresponding polyphosphazenes.

The Pt-catalyzed polymerization of neat 1,3-tetraethoxy-1,3-disilacyclobutane yields the hydrolytically sensitive polymer $[Si(OEt)_2CH_2]_n$. The degree of polymerization was determined after reduction of the polymer to polysilaethylene with $LiAlH_4$ in THF. It was found to be about 110–120, with a narrow polydispersity.
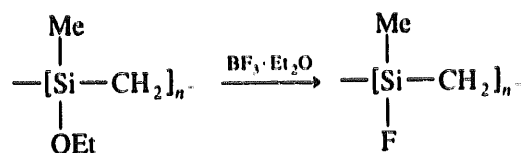
The necessary monomer for the preparation of poly[bis(trifluoroethoxy)silylenemethylene], tetrakis(trifluoroethoxy)disilacyclobutane, was conveniently prepared from TCDSCB (see section on monomer synthesis above) by reaction with a four-fold excess of trifluoroethanol. Polymerization of this neat monomer by chloroplatinic acid at 100°C gave the desired polymer, which turned out to be a hard, solid material that was only slightly soluble in THF and acetone. Both of these dialkoxy-substituted polymers are highly crystalline materials with no T_g and T_m = 31°C for the $[Si(OEt)CH_2]_n$ polymer and T_m = 134°C for the $[Si(OCH_2CF_3)_2CH_2]_n$ polymer. In contrast, poly(diethoxyphosphazene) is apparently an amorphous material with a T_g of −84°C. Poly[bis(trifluoroethoxy)phosphazene], however, is crystalline, with a T_g of −66°C and a T_m of 242°C; it also shows a disordering transition before melting that was not observed for the corresponding PSM [18].

2.5. Preparation of substituted PSMs by reactions with pre-formed polymers containing reactive Si–Cl and Si–H functionalities

By procedures based on those used in the well-developed hydrosilation chemistry of the corresponding polysiloxanes and the equally well-studied derivatization of poly(dichlorophosphazene), the polymers having Si–H groups described above (1 and 2), as well as the chloropolymer, poly(chloromethylsilylenemethylene) (3), can be used as starting materials for the synthesis of a wide variety of PSMs. In particular, we have found that the chloro group of polymer 3 can be quantitatively substituted by an OR group (where R = Et, CH_2CF_3, Ac, Ph) by reaction with a $ROH-Et_3N$ mixture or with RONa in ether or THF solution [19–21]:

$$
\begin{array}{ccc}
\text{Me} & & \text{Me} \\
| & \xrightarrow[\text{or NaOr}]{ROH-Et_3N} & | \\
-[Si-CH_2]_n\text{-} & & -[Si-CH_2]_n\text{-} \\
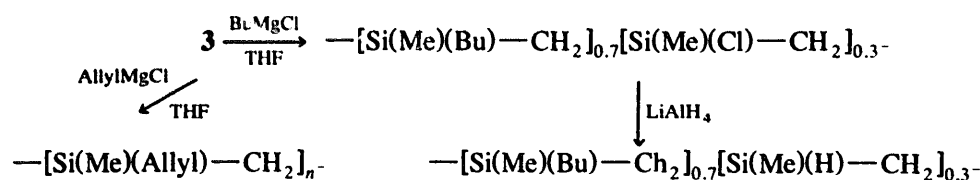| & & | \\
Cl & & OR \\
\mathbf{3} & &
\end{array}
$$

The reaction was complete after several hours of refluxing. All of the polymers showed some hydrolytic sensitivity, which varied with the OR group, in the following order: OPh < OCH_2CF_3 < OEt < OAc. The phenoxy-substituted polymer showed the highest hydrolytic stability, crosslinking only after 2–3 months of storage in air. The ethoxy-substituted polymer can be modified further. After stirring of this polymer with $BF_3 \cdot Et_2O$ at room temperature overnight, the apparently hydrolytically stable $[Si(F)(Me)CH_2]_n$ polymer was obtained in quantitative yield [21]:

$$
\begin{array}{ccc}
\text{Me} & & \text{Me} \\
| & \xrightarrow{BF_3 \cdot Et_2O} & | \\
-[Si-CH_2]_n\text{-} & & -[Si-CH_2]_n\text{-} \\
| & & | \\
OEt & & F
\end{array}
$$

Alkylation of polymer 3 was also attempted. Initial attempts to alkylate 3 using lithium reagents failed, giving only crosslinked products. This can be attributed to the occurance of a competing reaction involving proton abstraction from the bridging carbon followed by attack of the formed carbanion on the Si–Cl group, thus leading to crosslinking [21]:

$$
\mathbf{3} \xrightarrow{RLi} -[Si(Me)(Cl)-\bar{C}H]_n- \xrightarrow{-[Si(Me)(Cl)CH_2]_n-} \text{Crosslinked product}
$$
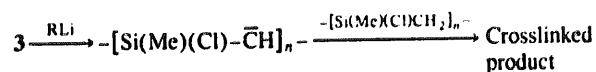
Next, alkylation of 3 was attempted with Grignard reagents. As has been observed for sterically hindered chlorosilanes, Grignard reagents did not bring about complete alkylation of polymer 3. For example, after

$$3 \xrightarrow[\text{THF}]{\text{BuMgCl}} \quad -[\text{Si(Me)(Bu)}-\text{CH}_2]_{0.7}[\text{Si(Me)(Cl)}-\text{CH}_2]_{0.3}-$$

AllylMgCl / THF

LiAlH$_4$ ↓

$$-[\text{Si(Me)(Allyl)}-\text{CH}_2]_n- \qquad -[\text{Si(Me)(Bu)}-\text{Ch}_2]_{0.7}[\text{Si(Me)(H)}-\text{CH}_2]_{0.3}-$$

refluxing one equivalent of **3** with two equivalents of 1 M *n*-BuMgCl in THF for 24 h, followed by reduction of the unreacted chloro groups with LiAlH$_4$, only 77% of the Si atoms had Bu substituents, as determined by NMR spectroscopy.

The only exception was allylmagnesium chloride, which gave the completely substituted poly(allylmethylsilylenemethylene) [21].

The structure of these polymers was studied in detail by NMR spectroscopy. As with the α-carbon atom of the asymmetrically substituted polyolefins, the Si atom of the [Si(Me)(R)CH$_2$]$_n$ polymers is chiral. In the ^{1}H and ^{13}C spectra of the Si(Me)(R)CH$_2$]$_n$ polymers, the Si-CH$_2$-Si and Si-CH$_3$ groups show multi$_{1}$'e peaks caused by the presence of various diastereomeric sequences. These peaks were successfully assigned to the various possible diastereomeric sequences, and the relative intensities of the peaks revealed the atactic nature of these polymers.

In accord with their atactic structure, all these polymers are completely amorphous and show T_gs which vary widely, depending on the nature of the substituent on the silicon. Some properties of these polymers are shown in Table 4.

Reactions analogous to those described above were attempted with poly(dichlorosilylenemethylene) (**4**) [19,20]. Unfortunately, all attempts to replace the chloro groups by alkoxy failed; only highly crosslinked material was obtained, presumably because of the hydrolytic sensitivity of **4** coupled with its low solubility in common solvents.

Another reactive group on Si that can be used to advantage as a means of introducing a specific side chain onto a PSM backbone is hydrogen. Addition of an Si-H bond to an olefin, i.e. hydrosilation, is widely used for introducing a side chain onto a siloxane backbone through reaction of poly(hydridomethylsiloxane) with the appropriate olefin [23]. Analogous chemistry was employed for poly(methylsilylenemethylene) (**1**)
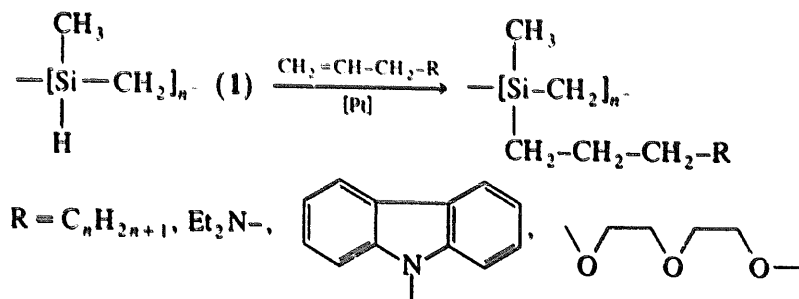
Table 4
Physical properties of the [Si(Me)(R)CH$_2$]$_n$ polymers

R	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	T_g
OEt	40.3	185.4	-79
OCH$_2$CF$_3$	— [a]	— [a]	-50.5
OAc	— [b]	— [b]	-28
OPh	24.7	172.2	-17.5
H	12.5	47.2	-101
F	66.8	192.2	-69
C$_3$H$_5$	2.4	6.8	-72
C$_4$H$_9$, H	11.7	39.6	-71

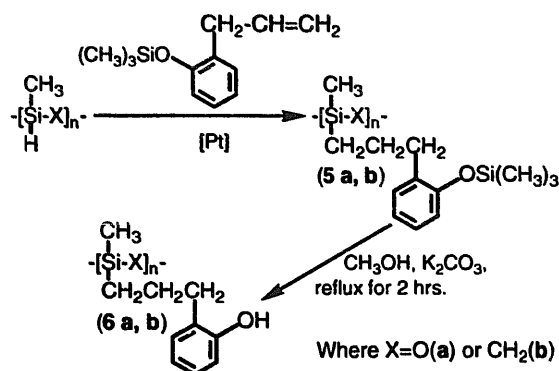[a] This polymer was not soluble in toluene, the solvent used for GPC measurements.
[b] Owing to its hydrolytic sensitivity, this polymer was not studied by GPC.

and several different side chains were successfully introduced on to the PSM backbone [22].

It was found that hydrosilation of **1** occurs with more difficulty than that of poly(hydridomethylsiloxane), always giving a lower degree of substitution than the corresponding polysiloxanes, perhaps because of the steric hindrance imposed by the two hydrogen atoms of the backbone methylene group. In addition, this steric hindrance makes the PSM backbone less flexible than the siloxane backbone, which accounts for the observation that the T_gs of the PSM polymers are typically 20-30°C higher than the those of the corresponding polysiloxanes.

Another difference between the polysiloxanes and the PSMs is the greater chemical stability of Si-C bond than of the Si-O bond. It is well known that the Si-O bond is susceptible to acid, and especially base, hydrolysis [23], while most Si-C bonds can be cleaved by acids and bases only under extreme conditions [24]. In order to evaluate the chemical stability of the PSMs compared to the polysiloxanes, base-soluble polymers of both types which contained a phenol group attached

CH$_3$
|
—[Si—CH$_2$]$_n$— (1) $\xrightarrow[\text{[Pt]}]{\text{CH}_2=\text{CH}-\text{CH}_2-\text{R}}$ —[Si-CH$_2$]$_n$-
|
H

CH$_3$
|
—[Si-CH$_2$]$_n$-
|
CH$_2$-CH$_2$-CH$_2$-R

R = C$_n$H$_{2n+1}$, Et$_2$N-,

to the Si by an alkyl bridge were synthesized as shown below:

Polymers **6a** and **6b** were dissolved in 10% aqueous KOH solution and the change in the molecular weights of the polymers (after recovery by adding acid) were monitored as a function of time of exposure to the basic medium. The results are summarized in Table 5.

From the data given in this table it can be seen that the substituted polysiloxane decomposes significan!ly, even in the presence of catalytic amounts of potassium carbonate, during the deprotection step. In contrast, the PSM derivative shows only slight decomposition during prolonged treatment with base.

3. PSMs as ceramic precursors

3.1. Pyrolysis of PSE to silicon carbide

In the 20 years since the work of Yajima et al. [25], which has led to the subsequent commercialization of Nicalon™ fiber, there has been considerable interest in the synthesis of polycarbosilanes and polysilanes that could serve as precursors to silicon carbide. Much of this work has been reviewed recently, and both the efforts to develop new precursors and to study the

Table 5
Hydrolytic stability of a substituted PSM compared with the corresponding poly[siloxane]

Polymer	X = O	X = CH₂
M_w of **5** (TMS protected)	18 200	19 100
M_w of **6**	5200	15 900
M_w of **6** calculated [a]	13 300	13 800
M_w of **6** after 24 h in 10% KOH at 25°C	1500	15 900
M_w of **5** after 120 h in 10% KOH at 25°C	—	13 000

[a] Assuming complete conversion of $-C_6H_4OSi(CH_3)_3$ into $-C_6H_4OH$.

chemistry of the pyrolytic conversion processes used in these cases to prepare SiC have been discussed in detail [26]. A key stage in this conversion process is the crosslinking, or thermosetting, step which converts the initially soluble or thermoplastic polymer into a solid that will hold its shape during the subsequent pyrolysis to SiC. Various well-known mechanisms for the formation of Si-Si or Si-C bonds have been investigated in this context [27-31]. Among these is the dehydrocoupling process that leads, at least initially, to the formation of Si-Si bonds between two Si-H groups. This process can be effected thermally [32] or catalytically [33,34], and is the basis of some polymer preparations [35,36] as well as many crosslinking processes in SiC precursor chemistry. The thermally induced elimination of H_2 from hydridopolycarbosilanes has been studied for several different polymer systems, including poly(silylethylene) (or polyvinylsilane) and poly(dimethylsilylethylene) [37], poly(methylsilane) [33] and poly(methylsilylenemethylene) (1), $[Si(Me)(H)CH_2]_n$ [4]. In the case of $[Si(Me)(H)CH_2]_n$, loss of hydrogen does not occur until ca. 400°C; this is then followed by a rapid decomposition between 400 and 500°C, giving a final ceramic yield of only ca. 10%. However, the ceramic yield was improved to 66% after thermal processing at 400°C, suggesting that the thermolysis of the relatively weak Si-H bond can provide a viable thermosetting mechanism for linear polycarbosilanes. Similarly, poly(methylsilane) $[-Si(H)(Me)-]_n$, which has Si-Si bonds as well as Si-H groups, crosslinks readily, either thermally or in the presence of the same dehydrocoupling catalyst used in its preparation, to provide a near stoichiometric SiC in high ceramic yield [33]. Moreover, recent work has shown that polymers which have two or three H atoms on Si apparently lose H_2 on heating even more readily, leading to higher ceramic yields and better retention of the initial Si_xC_y stoichiometry [17,37,38].

The availability of the parent member of the PSM series of polymers, PSE $[SiH_2CH_2]_n$, provides a unique opportunity to examine this H_2 elimination process, as well as the subsequent conversion of the crosslinked polymer to SiC, in the context of a relatively simple molecular structure having essentially only SiH_2 functionality available for crosslinking. Unlike most other examples of linear polycarbosilanes, which fragment on pyrolysis to yield volatile organosilanes with little or no ceramic residue, this polymer gives mainly H_2 as the volatile by-product on pyrolysis and is converted to stoichiometric SiC at 1000°C.

The conversion of PSE to SiC was studied in our laboratory [17,39] by analyzing both the volatile and solid products of pyrolysis at various stages in the conversion process. Analysis of the gaseous by-products of pyrolysis by mass spectrometry and gas chromatography indicate that H_2 is the major component. The onset

of H_2 evolution at ca. 300°C was signaled by the increase in the intensity of the peak at $m/e = 2$ above background levels. This peak reached an initial maximum at ca. 400°C and then went through at least two more maxima (at 480 and ca. 620°C) before dropping off in intensity beyond 800°C. In the case of the corresponding $[SiD_2H_2]_n$ polymer, loss of D_2 ($m/e = 4$) at a significant rate was observed starting at about the same temperature as the initial H_2 loss from the $[SiH_2CH_2]_n$ polymer; however, significant loss of H_2 did not occur until about 400°C.

Solid state NMR (^1H, ^{29}Si and ^{13}C), as well as FTIR, spectra were obtained from samples of the partially pyrolyzed polymer at various stages in the pyrolysis process. The ^1H NMR results show a pronounced broadening of both the SiH and CH resonances above 500°C, with a reduction in the intensity of the SiH_x relative to CH_x between 475 and 550°C. The onset of extensive structural rearrangement above ca. 500°C is also evident in the ^{29}Si, ^{13}C NMR and IR spectra. The ^{29}Si NMR spectrum for the 550°C sample shows a relatively broader, predominant, SiH_2 resonance at ca. −34 ppm, but also a significant peak at −12.9 ppm attributed to SiH groups. The Si–H stretching peak in the IR also broadens, and starts to shift to lower frequencies at 550°C, while a significant CH_3 peak (unobservable in the starting polymer) grows in. By 800°C, the SiH and CH peaks are no longer observable in the IR, and the ^{29}Si NMR spectrum shows a single, broad, peak at the expected position for SiC.

These observations are all consistent with the following two-stage mechanism for the pyrolysis of PSE to 1000°C [37]: (1) loss of H_2 from SiH_2 groups starting at ca. 300°C leads to crosslinking of the polymer and the formation of a network structure by ca. 450°C. The loss of H_2 from SiH_2 via a molecular elimination process is conceivable, which would form reactive silylene ($=Si:$) intermediates. These silylene species are known to insert readily into Si–H bonds, resulting in Si–Si bonds which, at elevated temperature, would quickly rearrange to the more stable Si–C–Si interchain linkages. (2) Extensive structural rearrangement, which is accompanied by loss of mainly H_2 but also some C- and Si-containing species, begins above 500°C, and is complete by at least 800°C, resulting in the conversion of the $[SiH_2CH_2]_n$ linear chain segments into a three-dimensional inorganic network. Free radical mechanisms are operative at this temperature range and cause further crosslinking as well as cleavage of the backbone Si–C bonds; however, owing to the preformed, crosslinked structure, extensive loss of low molecular weight chain fragments is prevented. The SiH_2 groups in this polymer therefore provide a latent reactivity that can be 'turned on' by heating, thereby allowing the formation of a network structure that resists fragmentation.
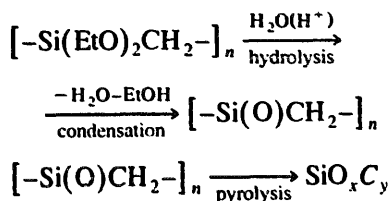
3.2. Preparation of a siloxy-methylene-bridged inorganic–organic network polymer and its conversion to silicon oxycarbide

Another important ceramic material is silicon oxycarbide. Owing to its excellent mechanical strength and toughness, its high temperature stability (up to ca. 1500°C), its resistance to oxidation and corrosion, and its amorphous character, silicon oxycarbide, having the general formula SiO_xC_y, would be expected to be a good material for many applications, including protective coatings [40]. The practical interest of this glass-like material is related to its increased thermochemical and thermomechanical stability compared with silica glass [41]. However, it appears to be quite difficult to retain carbon inside the silica network at the high temperatures involved in the traditional melting process; therefore, direct reaction of SiO_2 with carbon results in only a slight incorporation of carbon into $C(Si)_4$ sites. There have been a number of studies of the synthesis of silicon oxycarbide from polymeric precursors (silicones) [42,43]. Relative to the ceramic approach to the synthesis of SiO_xC_y, this new approach appears to provide both improved mechanical properties, owing to enhanced C incorporation into carbidic $[C(Si)_4]$ sites in the structure, as well as distinct processibility advantages. In this case, as in the case of the SiC precursors, extensive studies have been carried out employing various types of organosilicon precursor, as well as various approaches to their detailed study [43,44]. Our own efforts in this area have been directed towards enhancement of the carbidic carbon content through the use of organosilicon precursors that contain carbon initially bonded to more than one Si atom. This has led us to the study of both simple molecular alkoxycarbosilanes such as bis(triethoxysilyl)methane and tetramethoxydisilacyclobutane as well as polymeric carbosilanes in which, after hydrolysis, all of the carbon is present as CH_2 groups [43,45]. We will focus here on our study of poly(diethoxysilylenemethylene) as a sol-gel precursor to $[Si(O)CH_2]_n$ and its pyrolytic conversion to SiO_xC_y. Unlike most of the other precursor systems that have been studied in detail as SiO_xC_y precursors, this one is remarkably simple in terms of the Si and C microenvironments, thereby permitting a detailed study of the conversion of a polycarbosilane–siloxane into silicon oxycarbide.

The linear ethoxy-substituted polycarbosilane, poly(diethoxysilylenemethylene), was prepared as described above from the corresponding tertraalkoxydisilacyclobutane and converted into an inorganic–organic network polymer by the usual sol–gel method, with an acid catalyst (HCl). After drying and heating to 200°C to remove water and residual alcohol, a nearly completely condensed gel having a composition close to $[Si(O)CH_2]_n$ and the approximate structure

$[Si(O)CH_2]_m[Si(O)(OH)CH_2]_n$ ($m \gg n$) was obtained. The pyrolysis of this gel to silicon oxycarbide was then monitored by solid state NMR, IR, thermal analysis and gas product analysis methods. The relative simplicity of this initial gel structure allows us to track in detail the evolution of the SiO_xC_y structure as a function of temperature.

The reactions involved in this process are:

$$[-Si(EtO)_2CH_2-]_n \xrightarrow[\text{hydrolysis}]{H_2O(H^+)}$$

$$\xrightarrow[\text{condensation}]{-H_2O-EtOH} [-Si(O)CH_2-]_n$$

$$[-Si(O)CH_2-]_n \xrightarrow[\text{pyrolysis}]{} SiO_xC_y$$

Studies by thermogravimetric analysis and mass spectrometry show three regions of weight loss, from room temperature to 200°C (ca. 3%), from 200 to 600°C (ca. 6%) and from 600 to 1000°C (ca. 6%). The first weight loss below 200°C is attributed to loss of solvent and water. The other two stages are attributed to the completion of the condensation process and the decomposition of the polymer, respectively. The polymer gave a ca. 84% ceramic yield.

The ^{29}Si NMR spectrum of the dried gel shows three peaks at −59.9, −17.4 (major peak), and 8.2 ppm which can be assigned to $SiCO_3$ units (T), SiC_2O_2 units (D), and SiC_3O units (M). The respective chemical shift values for the T and D units are intermediate between the expected values for T_2 and T_1 units, and between the values for D_1 and D_2 units. This could arise from the presence of terminal oxygen ligands, such as –OH, bonded to Si. The presence of these uncondensed species is also evidenced by the OH and Si–O–H bands observed in the IR spectrum of the gel. Both solid state NMR (^{13}C and ^{29}Si) and IR spectra were obtained at various stages in the pyrolysis process and they all indicate the onset of significant structural changes at ca. 600°C. The weak IR peak due to the uncondensed Si–OH structure at 900 cm^{-1} decreased as the temperature increased and finally disappeared at 600°C, which is consistent with completion of the condensation process in this temperature range. There is a significant increase in the relative intensity of the band corresponding to the CH_3 structure at 1260 cm^{-1} (absent in the original PSM), as well as the Si–O structure at 1050 cm^{-1} and the Si–C structure at 800 cm^{-1}. The ^{29}Si solid state NMR spectra above 600°C show a decrease in the content of the SiC_2O_2 (D) unit, a significant increase in the content of the $SiCO_3$ (T) unit, and the emergence and increase of the SiO_4 (Q) unit, which is entirely absent from the initial gel structure.

All of these observations suggest that the environment of the silicon atoms during the heating of this material from ca. 600 to 1000°C has changed from that of a nearly pure SiC_2O_2 structure to a full distribution

of the five possible $SiC_{4-x}O_x$ environments. The reformation of the environments of the silicon atoms may be accounted for by the occurrence of a redistribution reaction involving the Si–O and Si–C bonds, which starts at ca. 500°C and reaches a metastable equilibrium state at ca. 900°C [44].

The free carbon content of the final SiO_xC_y glass, as calculated from the NMR and elemental analysis data, is 47.9% of the total carbon content. This is quite close to the expected 50%, assuming that, for the $(CH_2)SiO$ system, the O/Si ratio does not change during pyrolysis and the usual valences of C, Si, and O are maintained; therefore, 50% of the carbon should be lost or converted into free carbon [43]. Moreover, the O/Si ratios obtained from the elemental analysis and from quantitative solid state NMR, and the results of the distribution of $SiC_{4-x}O_x$ sites from experiment and from a statistical calculation based on the random distribution structural model [44] are also quite consistent.

In summary, these detailed studies of the linear PSM polymers has provided not only a better understanding of the structural changes during the polymer-to-ceramic conversion process for these two different types of polymer precursor, but has also given a unique perspective on the role of oxygen attached to Si in the initial polymer in determining the pyrolysis chemistry and thereby the composition of the ceramic end-product. It seems quite clear from these results that the thermodynamic stability of the Si–O bond, coupled with the availability of relatively facile Si–O/Si–C redistribution reactions, leads to effective retention of essentially all of the initial siloxy oxygen functionality and elimination from the final SiO_xC_{1-2x} network of any excess carbon.

Acknowledgements

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