

Linear and Hyperbranched Polycarbosilanes with Si-CH₂-Si Bridging Groups: A Synthetic Platform for the Construction of Novel Functional Polymeric Materials

L. V. Interrante, I. Rushkin and Q. Shen

¹Chemistry Department, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA

Work carried in the authors' laboratory on Si-CH₂-Si bridged polycarbosilanes is reviewed. In pursuit of high-yield polymeric precursors to silicon carbide, convenient synthetic routes to both linear and hyperbranched polycarbosilanes having a '[SiH₂CH₂]_n' compositional formula have been developed. The linear [SiH₂CH₂]_n polymer was prepared by ring-opening polymerization of a substituted disilacyclobutane, and was studied both as an analogue of polyethylene and as a high-yield precursor to SiC. Elaboration of the methods employed to prepare this polymer has yielded a wide range of new poly(silylenemethylene)s (PSMs) of the type [SiRR'/CH₂]_n, where R and R' can be a wide range of different groups, including a series of symmetrically disubstituted polymers with R = R' = F, alkyl and alkoxy which form crystalline solid phases and various amorphous, atactic polymers having different R and R' groups. By using (Si)-Cl replacement reactions analogous to those developed previously for polydichlorophosphazene, as well as hydrosilation reactions similar to those used for [Si(H)(Me)O]_n, a series of side-chain polymers having various groups attached to Si through Si-C or Si-O bonded linkages were obtained. Similar polymer modification reactions have recently been developed for the branched oligomer/polymer analogue of these linear polycarbosilanes, leading to hyperbranched species with functional substituents, including a di(ethyleneoxy) methyl ether-terminated derivative which readily dissolves lithium salts. The results of studies of these novel 'inorganic/organic' hybrid polycarbosilanes are described and their properties are compared with those of related carbon-backbone and

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INTRODUCTION

1.1 Polycarbosilanes as SiC precursors

During the last two decades, a major motivation for the synthesis and study of new polycarbosilanes has been the prospect of their use as pyrolytic precursors to silicon carbide (SiC). Among the key requirements for such SiC precursors have been: (1) processability, allowing the fabrication of continuous fibers, films etc.; (2) high conversion yield (ceramic yield) to high-purity SiC; and (3) the availability of a convenient crosslinking or thermosetting mechanism so as to allow retention of shape after processing and during pyrolysis. Various polycarbosilanes and polysilanes have been investigated for this purpose¹⁻⁸; however, the Yajima polycarbosilane, nominally '[SiH(CH₃)CH₂]_n', has generated particular interest, due in part to its application as a precursor in the production of the only commercial SiC fiber, Nicalon[®].¹ In this latter case the polymer employed, which is derived from [Me₂Si]_n by thermal isomerization, has a relatively high ratio of C to Si (2:1) and a complex structure which appears to contain largely carbosilane linkages. Much of this excess carbon ends up in the ceramic product on pyrolysis, leading to decreased oxidative stability, poor crystallinity and less than fully satisfactory mechanical properties.

* Correspondence to: L. V. Interrante, Chemistry Department, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA.
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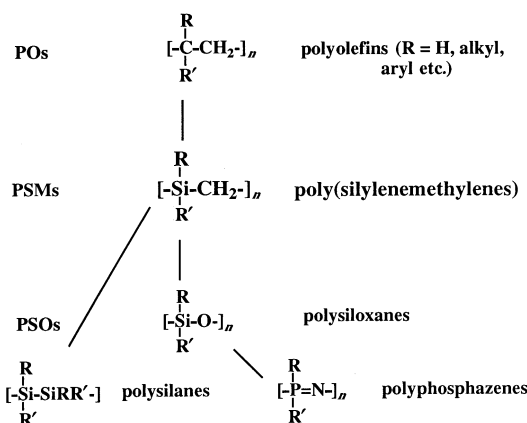
Most of the other polycarbosilanes and polysilanes that have been studied also contain excess carbon; either this must be eliminated on pyrolysis, resulting in a lower ceramic yield, or (more usually) it ends up in the ceramic product as free carbon.¹⁻⁸

The one exception is polymethylsilane, $[\text{SiH}(\text{CH}_3)]_n$, which has been produced from the corresponding dichloromethylsilane by alkali-metal (Wurtz) coupling⁴ or by dehydropolymerization of methylsilane with transition-metal complex catalysts.⁵ In this case, there is typically some methane loss on pyrolysis, leading to silicon-rich SiC. Moreover, the polymer is pyrophoric, requiring extreme care in its handling in order to avoid oxygen incorporation.

1.2 The Poly(silylenemethylene)s (PSMs)

As is clear from the case of polymethylsilane, the use of a polymer that has an Si/C ratio of 1:1 but where the carbon is contained in a pendant $-\text{CH}_3$ group does not necessarily lead to a ceramic product which retains the Si/C 1:1 starting ratio. A potential solution to this loss of carbon on pyrolysis is to incorporate it as a bridging methylene group in the polymeric structure where it is effectively 'locked' between two silicon atoms. Polycarbosilanes which have the average composition $[\text{SiH}_2\text{CH}_2]_n$ obviously fulfill both of the objectives of an initial 1:1 stoichiometry and a bridging carbon. One such polymer having both this composition and (presumed) linear structure was reported in a Patent in 1986.⁹ This was obtained by ring-opening polymerization of disilacyclobutane (DSCB) with H_2PtCl_6 (a procedure now known to induce crosslinking via Si-H bond activation¹⁰) and was reported to yield silicon carbide in 85% yield on pyrolysis to 900°C. This polymer can be viewed as the 'parent' of a class of polymers called the poly(silylenemethylene)s (PSMs), having the general formula, $[\text{Si}(\text{R})(\text{R}')-\text{CH}_2]_n$. From the standpoint of their molecular structure, the PSMs occupy a unique place among the known examples of linear polymeric materials and, in fact, they can be viewed as a class of inorganic/organic hybrid polymers that effectively bridge the gap between the purely organic backbone polyolefins (POs) and such inorganic backbone polymers as the polysiloxanes (PSOs), polysilanes and polyphosphazenes (PPPs) (Scheme 1).

In this context, a comparison of the properties of selected PSMs with those of analogous 'organic' and 'inorganic' polymers could shed light on the



Scheme 1 Relationship between the PSMs and other linear polymers.

structure-property relationships in all these polymers. One of the objectives of our research has been to explore these relationships through the synthesis and study of analogously substituted PSMs, POs and PSOs.

The best method available for the preparation of linear polycarbosilanes having a regular $[-\text{Si}-\text{C}-\text{C}-\text{C}]_n$ or $[-\text{Si}-\text{C}]_n$ structure is the ring-opening polymerization (ROP) of the corresponding mono- and di-silacyclobutanes (DSCBs). This ROP has been carried out both thermally and catalytically with various platinum complexes and other late-transition-metal compounds.¹¹⁻¹⁸ Anionic polymerization of silacyclobutanes employing alkyl-lithiums has also been used successfully to prepare certain polycarbosilanes; however, in the case of the DSCBs this method has received relatively little attention in the literature.¹⁹⁻²² For the transition-metal-catalyzed polymerization, the most likely mechanism appears to involve oxidative addition of the mono- or di-silacyclobutane to the metal [most likely Pt(0)] to form a metallocyclic intermediate which presumably then goes on to react with more monomer, either to expand the ring or to grow a linear polycarbosilane chain from the metal center.^{23,24}

In the case of the disilacyclobutanes, the resultant poly(silylenemethylene)s (PSMs) can have either the same or different substituents on the Si, leading to possible crystallization of the polymer chains in the case of the $\text{R} = \text{R}'$ derivatives, or to chiral silicon centers — and thereby different possible configurational sequences — when R and R' are different groups. In the initial studies of the PSMs obtained by ROP, the silicon substituents were relatively simple alkyl or aryl groups and little

effort was made to examine the stereochemical consequences of different silicon substituents or to investigate crystallization.^{11–18} Indeed, except for poly(dimethylsilylenemethylene), which was the first PSM to receive attention and for which only glass formation has been evidenced on cooling, until quite recently very little attention has been directed to the investigation of the detailed molecular structure and ordering phenomena in these polymers. In the last few years, in addition to the work described below, various other groups have contributed to a growing interest in such PSMs.^{24–33}

2 SYNTHESIS OF HYPERBRANCHED AND LINEAR POLYMERS OF FORMULA '[SiH₂CH₂]_n'

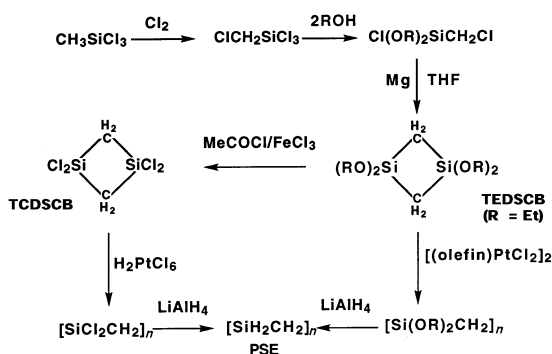
2.1 The linear [SiH₂CH₂]_n polymer

In pursuit of precursors to stoichiometric SiC, we have investigated two routes to polycarbosilanes having a 'SiH₂CH₂' compositional formula. One of these routes¹⁰ starts with tetrachlorodisilacyclobutane (TCDCSB) and involves a platinum-catalyzed ring-opening polymerization, followed by LiAlH₄ reduction, to yield the linear polysilaethylene, [SiH₂CH₂]_n (PSE) (Scheme 2). A polymer of this type was presumably obtained previously by direct ROP of DSCB⁹; however, our efforts to reproduce this synthesis yielded an intractable product, presumably due to the activation of the Si–H bonds by the platinum catalyst¹⁰.

Initially, the monomer for this polymerization, TCDCSB, was synthesized by the gas-phase

pyrolysis of 1,1-dichloro-1-silacyclobutane¹⁰. This rather cumbersome procedure was improved considerably by the discovery of a more convenient route to TCDCSB through the corresponding tetraethoxydisilacyclobutane (TEDSCB) (Scheme 2). The starting material in this synthesis is the relatively inexpensive methyltrichlorosilane, which was converted to chloromethyltrichlorosilane and then to the chloromethyldiethoxychlorosilane in good yield by using modifications of previously reported synthetic procedures. This conversion of the latter compound to the disilacyclobutane also follows the general method reported by Kriner for the synthesis of various substituted DSCBs¹⁸. The conversion of the tetraethoxy-DSCB to the TCDCSB was successfully carried out by using acetyl chloride as the chlorination reagent. The total yield from Cl₃SiCH₂Cl to TCDCSB was about 30%, which is higher than that obtained from the pyrolysis of dichlorosilacyclobutane. Moreover, the reaction is amenable to scale-up and the procedures involved are easier to carry out.

Polymerization of TCDCSB was conducted in benzene at 90 °C using chloroplatinic acid. After the reaction mixture had gelled, Et₂O was added and the [SiCl₂CH₂]_n polymer was reduced by LiAlH₄ to yield PSE after aqueous work-up. A sample of the PSE prepared by this method starting from a commercial source of methyltrichlorosilane was examined in detail by solution NMR methods, leading to a complete characterization of its molecular structure as well as an independent estimate of the average molecular weight³⁴. The results were, in general, consistent with a regularly alternating -SiH₂CH₂- structure terminated by -CH₃ and -SiH₃ end-groups and a degree of polymerization of ca 250 (*M_n* ≈ 10 000 a.m.u.). The same sample gave a gel-permeation chromatography (GPC)-determined [polystyrene (PS) standards] *M_n* of ca 20 000, suggesting that the GPC value tends to overestimate the true molecular weight by a factor of as much as two. Moreover, the NMR results also indicated the presence in the molecular structure of a small concentration (approx one per polymer chain) of (H)SiC₃ branch sites. Various possible sources for this branching site were examined by copolymerizing the corresponding monomers with the TCDCSB. These included trichloro-DSCBs having a single -CH₂SiCl₃ or -CH₃ group attached to Si. Both monomers were successfully copolymerized with an approx ten-fold excess of TCDCSB and then reduced with LiAlH₄ to yield the corresponding [Si(H)(CH₂SiH₃)CH₂]_x[SiH₂CH₂]_{l-x} and [Si(H)(Me)CH₂]_x[SiH₂CH₂]_{l-x}.



Scheme 2 New route to PSE and related polycarbosilanes.

random copolymers with $x \simeq 0.1$. The latter, methyl-substituted, PSE was found to have extra peaks in its ^1H , ^{13}C and ^{29}Si NMR spectra that were identical to those observed for the original PSE sample. The origin of this methyl branching in the original PSE was concluded to arise from the small amount of Me_2SiCl_2 in the MeSiCl_3 starting material, which undergoes chlorination to give $\text{MeSi}(\text{CH}_2\text{Cl})\text{Cl}_2$.

An alternative way of preparing PSE is via ROP of tetraethoxydisilacyclobutane, followed by LiAlH_4 reduction (Scheme 2). The resultant product has a lower molecular weight ($M_w = 7000$) than the version obtained from TCDSCB, presumably due to a less effective ROP in the case of TEDSCB.

PSE has an extraordinarily high ceramic yield of 86–90% by thermogravimetric analysis (TGA) (the theoretical yield of SiC is 91%) and retains its initial Si/C 1:1 ratio on pyrolysis to give a nanocrystalline β -SiC at 1000 °C. Therefore, despite its relatively high cost, PSE is a useful model system for the study of the precursor-to-ceramic conversion process, because of its simple, highly regular and well-defined molecular structure.

We have employed both gas-phase analyses (by mass spectrometry) and analysis of the intermediate solids at various temperatures to follow the conversion process.³⁵ Over 90% of the gaseous product is dihydrogen with traces of methane, C_2 hydrocarbons and methylsilanes. Studies of the $[\text{SiD}_2\text{CH}_2]_n$ polymer show that the initial loss of hydrogen which accompanies crosslinking between *ca* 300 and 400 °C is almost entirely from the hydrogen that is attached to Si. This is accompanied by changes in the NMR and IR spectra that suggest that Si–C network formation begins in this temperature range to lead to a partially crosslinked structure containing (SiC_3H) sites. As has been done previously in the case of poly(silylene)³⁶, we attribute the crosslinking in this stage of the conversion process to 1,1- H_2 elimination reactions which lead to highly reactive silylene sites, followed by interchain Si–H insertion and, finally, rearrangement of the Si–Si linkages to carbosilane links by the Kumada rearrangement. This produces a partially crosslinked network structure which then resists fragmentation to volatile by-products in the 450–600 °C region where homolytic Si–C bond breakage starts to become important. It seems likely that a similar mechanism is operative in the case of the hyperbranched system, HBPSE, which has both SiH_2 and SiH_3 groups that can participate in 1,1- H_2 elimination. Previous studies of polymers that have only one H atom on Si have shown that at least two

H atoms per Si are needed for this crosslinking mechanism to be effective in hydridopolycarbosilanes³⁷.

2.2 Preparation of a highly branched version of $[\text{SiH}_2\text{CH}_2]_n$

Another 'polymer' with a $[\text{SiH}_2\text{CH}_2]$ composition was prepared by Grignard coupling of $\text{ClCH}_2\text{SiCl}_3$ (obtained from CH_3SiCl_3 by chlorination in 75% yield), followed by LiAlH_4 reduction^{38,39}. This procedure leads to a highly branched polymer/oligomer mixture with a $[\text{H}_3\text{SiCH}_2]_w[\text{H}_2\text{SiCH}_2]_x[\text{HSiCH}_2]_y[\text{SiCH}_2]_z$ structure, which we have called Hyper Branched PolySilaEthylene, or HBPSE⁴⁰. The relative amounts of the different units which comprise this polymer were evaluated by ^{29}Si NMR spectroscopy. It was found that $w/x/y/z \approx 11:20:8:2$.^{38–40} Analysis of the molecular-weight distribution of this product by GPC coupled with vapor-pressure osmometry^{38–40} suggested a typical $M_w/M_n = 1000:600$, corresponding to an average degree of polymerization of about 13. This SiC precursor (known commercially as HPCS) and its partially allyl-substituted derivative, AHPCS, have proven useful as SiC matrix sources for SiC fiber and particulate-reinforced SiC/SiC composites^{41,42}. Its fluidity, ability to undergo thermal crosslinking, high ceramic yield and moderate stability in air have been particularly advantageous in processing such composites, and recent improvements in the synthesis method (Q. Shen and L. V. Interrante, unpublished work) have allowed its production in large quantities (up to 6 liters/batch).

3 PREPARATION OF NEW SUBSTITUTED POLY(SILYLENEMETHYLENE)S

A series of new symmetrically disubstituted and asymmetrically monosubstituted PSMs have been obtained by employing various modifications of procedures previously described for the syntheses of substituted DSCBs, as well as by reactions on pre-formed polymers bearing reactive functional groups.

3.1 Preparation of symmetrically disubstituted PSMs

Among the new polymers that were prepared by ROP of the correspondingly substituted DSCBs

were a series of symmetrically disubstituted *n*-alkyl derivatives of the type $[\text{SiR}_2\text{CH}_2]_n$, R = (ethyl to *n*-hexyl). These polymers were found to be crystalline at low temperatures, as evidenced by differential scanning calorimetry (DSC) and (WAXD) measurements. In these cases an unusual first-order transition was observed just prior to melting to an isotropic liquid in the range 55–96 °C (similar results from a parallel investigation of these polymers have recently been reported.^{28,31} These unusual transitions preceding melting are reminiscent of the transitions previously observed by DSC, WAXD and other methods in the case of the corresponding dialkyl-substituted polysiloxanes $[\text{SiR}_2\text{O}]_n$, R = (ethyl to *n*-hexyl), which were attributed to partial disordering of the $[\text{SiR}_2\text{O}]_n$ chains prior to melting.^{44–46} In the mesomorphic state the chains are believed to be fully disordered along the chain direction but still arranged laterally in a columnar hexagonal structure. Similar transitions to a partially disordered state have also been observed for polysilanes of the type $[\text{SiR}_2]_n$,^{47,48} and for certain polyphosphazenes.^{49,50} In the case of the polysilanes, the absorption maximum which has been attributed to σ -conjugation in the Si–Si backbone shifts substantially as a result of the disordering transition, which has therefore been described as thermochromic. In the case of the PSMs, perhaps because of the much narrower temperature range for the intermediate phase, efforts to characterize an intermediate mesogenic phase have so far been unsuccessful.

A similar approach was used to prepare the first dialkoxy-substituted PSMs, $[\text{Si}(\text{OR})_2\text{CH}_2]_n$, where R = CH_2CH_3 and CH_2CF_3 .⁵¹ In these cases, DSC measurements again indicated crystallinity, with the T_m for R,R' = OCH_2CF_3 (135 °C) substantially higher than that for R,R' = OEt (31 °C). These dialkoxy-substituted polymers have no analogues among the known polysiloxanes but in some respects resemble the corresponding polyphosphazenes. However, whereas both of these dialkoxy-substituted PSMs are highly crystalline, the corresponding poly(diethoxyphosphazene) is apparently amorphous with a T_g of –84 °C. Poly[bis(trifluoroethoxy)phosphazene], on the other hand, is semicrystalline, with a T_g of –66 °C and a T_m of 242 °C.⁵¹ It also shows a disordering transition before melting, which was not observed for the corresponding PSM.

The diethoxy-PSM undergoes hydrolysis and condensation when treated with $\text{H}_2\text{O}/\text{HCl}$ in ethanol to give a siloxy/methylene-bridged gel.^{52,53} Pyrolysis of this gel to 1000 °C yields

silicon oxycarbide (SiO_xC_y), an amorphous ceramic material that can be considered as a hybrid of SiO_2 glass and SiC, with some of the carbon in tetrahedral Si_4C sites. This material has been of interest as a matrix phase for ceramic composites and as a hard coating for various substrates. Similar 'sol-gel' chemistry can be carried out with the ethoxy-substituted polymer/oligomer system obtained from the preparation of the hyperbranched polycarbosilane, yielding a related $[\text{Si}(\text{O})\text{CH}_2]_n$ gel in which the Si atoms occur in various $[\text{O}_x\text{Si}(\text{CH}_2)_{4-x}]$ ($x = 0–3$) environments bridged by both -O- and - CH_2 - groups.⁵³ The latter system has been used as a sol-gel precursor for the preparation of SiO_xC_y coatings.⁵⁴

3.2 Preparation of PSMs by replacement reactions on pre-formed polymers.

3.2.1 Replacement of (Si)-Cl on

$[(\text{Me})\text{Si}(\text{Cl})\text{CH}_2]_n$

Unlike the PSOs, where polymers containing Si-X (X = halogen, OR, NHR etc.) groups are either not readily available or too unstable to use as starting materials for polymer grafting reactions, PSMs which contain one or two Si-X (X = Cl, OR) groups can be readily prepared by ROP of the respective DSCB monomers, and the resulting polymers can be used as starting materials for the preparation of a wide range of new polymers. The preparation of PSE from both the $[\text{SiCl}_2\text{CH}_2]_n$ and $[\text{Si}(\text{OEt})_2\text{CH}_2]_n$ polymers (Scheme 2) provides a good illustration of this approach in the case of the disubstituted $[\text{SiX}_2\text{CH}_2]_n$ polymers. Various substituted PSMs were obtained by using the $[\text{Si}(\text{Me})(\text{Cl})\text{CH}_2]_n$ polymer, which is easily prepared in high-molecular-weight form from the corresponding DSCB and which is readily soluble in a wide range of organic solvents, including ethers and aromatic hydrocarbons. By using both the corresponding alcohol and triethylamine or the sodium alkoxide salt, various monoalkoxy-substituted PSMs of the type $[\text{Si}(\text{Me})(\text{OR}')\text{CH}_2]_n$, where R' = Et, CH_2CF_3 , Ph, COCH_3 (Ac), were obtained with apparently 100% substitution.^{51,55} These polymers show quite variable hydrolytic stability, which ranges from relatively rapid hydrolysis in moist air to stability in contact with liquid water for an indefinite period from R' = Ac to Ph, in the approximate order $\text{Ac} < \text{Et} < \text{CH}_2\text{CF}_3 < \text{Ph}$. Attempts to alkylate the $[\text{Si}(\text{Me})(\text{Cl})\text{CH}_2]_n$ polymer by using organolithium reagents led to crosslinking (presumably through attack of the lithium reagents on the main-chain

methylene groups); however, the use of Grignard reagents, RMgX ($\text{R} = n\text{-C}_4\text{H}_9$, allyl), proved somewhat more successful, leading to *ca* 70% substitution in the $\text{R} = \text{Bu}$ case and complete replacement of Cl by $\text{CH}_2=\text{CHCH}_2-$ in the case of $\text{R} = \text{allyl}$.⁵⁵

3.2.2 Replacement of alkoxy by fluoro: preparation of the first Si-F polymers

Both the $[\text{Si}(\text{Me})(\text{OEt})\text{CH}_2]_n$ and $[\text{Si}(\text{OEt})_2\text{CH}_2]_n$ polymers were used in F-for-OR replacement reactions by using $\text{Et}_2\text{O}/\text{BF}_3$.^{51,56} In the case of the resulting $[\text{SiF}_2\text{CH}_2]_n$ polymer, an apparently identical (except perhaps for a lower molecular weight) material was also obtained by direct ROP of the corresponding tetrafluoro-DSCB. These fluoro-substituted polycarbosilanes are apparently the first organosilicon polymers that contain F directly bonded to Si.

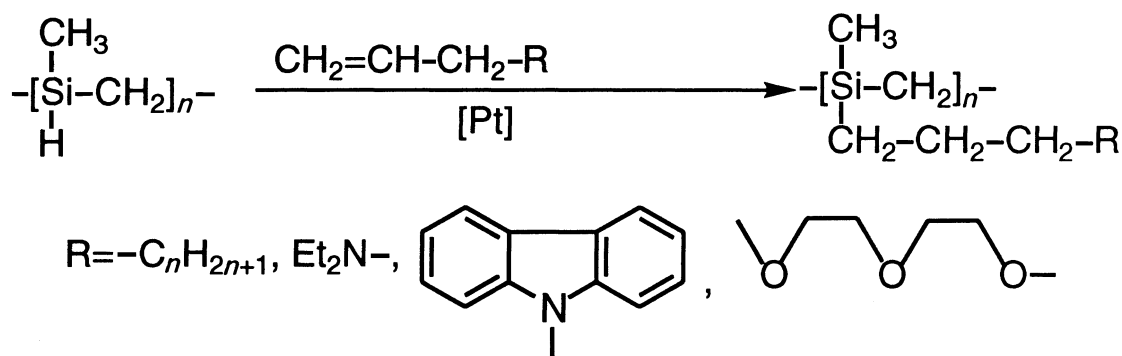
The $[\text{Si}(\text{Me})(\text{F})\text{CH}_2]_n$ polymer,⁵¹ like its chloro analogue, is readily soluble in common organic solvents such as aromatic hydrocarbons and chloroform and is apparently not very sensitive towards hydrolysis, surviving direct contact with water in the neat or solution state as well as atmospheric exposure for extended periods. This polymer was fully characterized by high-resolution NMR methods, which provided evidence for an atactic structure where the diastereomeric sequences formed by the chiral silicon atoms in the polymer chain, as well as (Si)-F coupling, cause splitting of the peaks of the main-chain nuclei and the SiCH_3 group.

The corresponding difluoro-substituted PSM, $[\text{SiF}_2\text{CH}_2]_n$, which is a Si analogue of the scientifically and commercially important organic polymer poly(vinylidene fluoride) (PVF_2), is apparently completely insoluble in all solvents tried, including several which do dissolve PVF_2 .²⁶ This polymer does undergo hydrolysis on standing in moist air or when treated with solvents that contain

water, which complicated early efforts to prepare and characterize it. Eventually, a product which appears to have all but a few per cent of its Si atoms in the form of SiF_2 units was obtained by extended refluxing in an excess of $\text{Et}_2\text{O}/\text{BF}_3$ and characterized by means of solid-state NMR and IR measurements. These data were consistent with expectations for a regularly alternating $-\text{SiF}_2\text{CH}_2-$ structure with less than 9% of the Si in the form of SiO_2C_2 units. The solid polymer obtained exhibits a multi-line X-ray diffraction (XRD) pattern; this pattern has been indexed by an orthorhombic unit cell which has a *c*-axis dimension of 3.30 Å (B. Farmer, University of Virginia, private communication). This is very close to the calculated repeat distance for a $[\text{SiF}_2\text{CH}_2]_n$ chain in the all-*trans*, planar zig-zag conformation, which is the conformation exhibited by PVF_2 in the crystalline form that shows the highest piezoelectric (and pyroelectric) properties and which maximizes the net chain dipole moment. Unlike PVF_2 , $[\text{SiF}_2\text{CH}_2]_n$ (at least so far) is insoluble and undergoes thermal decomposition (depolymerization) at around 250 °C. It does show a relatively sharp endothermic peak in the DSC at around 140–170 °C, which may be due to a solid-solid phase transition. Efforts to characterize this novel analogue of PVF_2 further, and to determine whether this analogy extends to its electrical/dielectric properties, are continuing, as are efforts to improve the synthesis of this polymer so as totally to avoid hydrolysis and thereby formation of Si-O-Si interchain crosslinks.

3.2.3 Hydrosilation by using $[(\text{Me})\text{Si}(\text{H})\text{CH}_2]_n$

In the case of the polysiloxanes, the main method that has been available for the structural modification of pre-formed polymers is hydrosilation of the $[\text{Si}(\text{H})(\text{Me})\text{O}]_n$ polymer. This method has been used for many years to provide a wide range of different side-chain polysiloxanes, including side-



Scheme 3 Hydrosilation as a route to side-chain PSMs.)

chain liquid-crystalline polymers.⁵⁷ The corresponding PSM, $[\text{Si}(\text{H})(\text{Me})\text{CH}_2]_n$, is readily available from the chloro polymer by reaction with LiAlH_4 and has been used in a series of hydrosilation reactions on various olefins, including 1-hexene and various allyl-terminated compounds of the type $\text{CH}_2=\text{CHCH}_2\text{R}$ (Scheme 3).⁵⁸ These reactions were catalyzed by using Karstedt's catalyst and proceed in high yield (80–95%) at a somewhat slower rate (and with a slightly lower extent of reaction) than with the corresponding siloxane.

RELATIONSHIP OF THE POLY(SILYLENEMETHYLENE)S WITH OTHER POLYMERIC MATERIALS

4.1 Relationship between PSE and polyethylene (PE)

In addition to its interest as a high-yield precursor to SiC, the linear polymer, PSE, is also of interest as an analogue of the commercially important polyethylene (PE). Unlike PE, which is a highly crystalline polymer that melts at around 140 °C, PSE is obtained as a viscous liquid which crystallizes on cooling below 0 °C. Optical microscopy of the solid phase shows a spherulitic structure indicative of a partially crystalline polymer.⁵⁹ WAXD and IR/Raman studies, along with the results of solid-state NMR studies, have revealed that the PSE chains occur in a planar zig-zag conformation in the solid state, packing in a unit

cell having dimensions $a = 5.70 \text{ \AA}$, $b = 8.75 \text{ \AA}$, $c = 3.25 \text{ \AA}$ and $\gamma = 97.6^\circ$.⁶⁰ *Ab initio* Hartree–Fock (6–31 g*) calculations were performed on the model system $\text{H}_3\text{SiCH}_2\text{SiH}_2\text{CH}_2\text{SiH}_3$ to determine the torsional surface for the two dihedral angles containing the heavier atoms of the system.⁵⁹ A relatively flat torsional surface was obtained with the all-*trans* (*t,t*) form as the global minimum and the corresponding g^+,g^+ form (with dihedral angles = 62°, 62°) only 1.26 kJ mol⁻¹ higher in energy. A general similarity to the torsional surface for the corresponding n-pentane was observed, but with a considerably flatter surface overall for the carbosilane. The barrier for rotation about the internal Si–C bonds (converting the *t,t* to the *t,g^+* form) was found to be 4.5 kJ mol⁻¹. The low torsional barrier in this carbosilane compared with that calculated for n-pentane (14.6 kJ mol⁻¹) was attributed to the greater length of the Si–C (1.89 Å) and Si–H (1.49 Å) bonds compared with the C–C (1.53 Å) and C–H (1.10 Å) bonds. This significantly reduces the repulsive interactions between the substituents. The Hartree–Fock surface was input as a reference function for the dihedral energetics and the single-chain conformational statistics were explored using Monte Carlo methods. The relatively more coiled form found for PSE than for PE, as is indicated by its smaller characteristic ratio (5.26 compared with 6.75), suggests a higher entropy of fusion for PSE, consistent with its lower melting point.

Similar considerations can be applied in considering the likely effects of changes in the chain backbone constituents on the glass transition temperatures of comparably substituted, atactic POs, PSMs and PSOs. In comparison with the

Table 1 T_g values for related POs, PSMs and PSOs

Polyolefin	T_g (°C)	PSM	T_g (°C)	Polysiloxane	T_g (°C)
$[\text{CH}(\text{Me})\text{CH}_2]_n$	-10 to -20 ^a	$[\text{SiMe}(\text{H})\text{CH}_2]_n$	-112 ^b		
$[\text{CMe}_2\text{CH}_2]_n$	-70 ^d	$[\text{SiMe}_2\text{CH}_2]_n$	-87 ^b	$[\text{SiMe}_2\text{O}]_n$	-126 ^c
$[\text{CH}(\text{Et})\text{CH}_2]_n$	-25 ^a	$[\text{SiMe}(\text{Et})\text{CH}_2]_n$	-78.2 ^b	$[\text{SiMe}(\text{Et})\text{O}]_n$	-139 ^c
$[\text{CH}(\text{nPr})\text{CH}_2]_n$	-40 ^a	$[\text{SiMe}(\text{nPr})\text{CH}_2]_n$	-61.2 ^b	$[\text{SiMe}(\text{nPr})\text{O}]_n$	-120 ^c
$[\text{CH}(\text{nBu})\text{CH}_2]_n$	-50 ^a	$[\text{SiMe}(\text{nBu})\text{CH}_2]_n$	-63.0 ^b	$[\text{SiMe}(\text{nBu})\text{O}]_n$	-115 ^c
		$[\text{SiMe}(\text{nPe})\text{CH}_2]_n$	-64.9 ^b	$[\text{SiMe}(\text{nPe})\text{O}]_n$	-112 ^c
$[\text{CH}(\text{nHex})\text{CH}_2]_n$	-65 ^a	$[\text{SiH}(\text{nHex})\text{CH}_2]_n$	-91.4 ^b		
		$[\text{SiMe}(\text{nHex})\text{CH}_2]_n$	-71.1 ^b	$[\text{SiMe}(\text{nHex})\text{O}]_n$	-108 ^c
$[\text{CH}(\text{Ph})\text{CH}_2]_n$	100 ^e	$[\text{SiH}(\text{Ph})\text{CH}_2]_n$	-37.6 ^b		
$[\text{CMe}(\text{Ph})\text{CH}_2]_n$	168 ^e	$[\text{SiMe}(\text{Ph})\text{CH}_2]_n$	28.6 ^b	$[\text{SiMe}(\text{Ph})\text{O}]_n$	-30 ^f

^a Ref. 63.

^b Ref. 61.

^c Ref. 64.

^d Ref. 65.

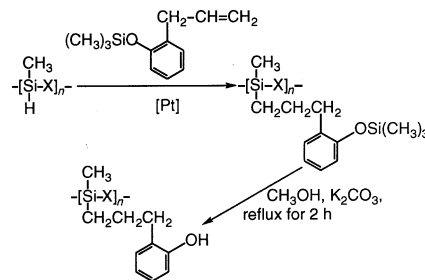
^e Ref. 66.

^f Ref. 67.

polyolefins, the longer Si–C bond of the PSMs might be expected to result in lower T_g values for the corresponding amorphous (atactic) polymers, whereas in comparison with the PSOs, the PSMs should have higher T_g s, due to the greater steric barrier for chain torsion imposed by the CH_2 groups relative to the bridging oxygen in the PSOs. Table 1 shows that these expectations are in fact realized for similarly substituted polymers of these three types. The respective PSM derivatives were all prepared by ROP of a *cis/trans* mixture of the appropriately substituted disilacyclobutanes, obtained from either the 'reverse-addition' Grignard reaction or the reaction of 1,3-dichloro-1,3-dimethyldisilacyclobutane and Grignard reagents (RMgX).⁶¹

The T_g values of three series of n-alkyl substituted polymers, $[\text{CHRCH}_2]_n$, $[\text{Si}(\text{Me})\text{RCH}_2]_n$ and $[\text{Si}(\text{Me})\text{RO}]_n$, where R = Et, n-Pr, n-Bu, n-Pe and n-Hex, were compared (Table 1).⁶² It is interesting to note that, unlike the polyolefins, where the T_g values decrease as the lengths of the alkyl side-chains increase, the T_g s of the corresponding PSOs, $[\text{Si}(\text{Me})\text{RO}]_n$, increase as the lengths of the alkyl side-groups increase. The PSMs exhibit a behavior intermediate between the two extremes of T_g continuously increasing or decreasing with side-chain length which was found for the polysiloxanes and polyolefins, respectively. These results suggest that the dominant factor that determines the T_g in the case of the polysiloxanes is the main-chain flexibility, and that the effect of adding alkyl groups of increasing size is to reduce this flexibility, and thereby the T_g , at least up to n-hexyl. On the other hand, for the polyolefins, where the main chain is much less flexible, the dominant effect of adding n-alkyl side-chains of increasing length is to decrease the cohesive energy between chains (or, equivalently, to increase the 'free volume'). The PSMs, with their intermediate chain flexibility, may lie in a range where these two effects compete with one another, producing first an increase in T_g from Et to n-Pr due to a reduction in the main-chain flexibility, and then a decrease in T_g beyond n-Pr as the effect of the side-chain mobility becomes increasingly important in the context of a less-mobile main chain.

In order to compare the chemical stability of PSMs and polysiloxanes, phenol-grafted polymers were prepared by hydrosilylation of TMS-protected allylphenol with $[\text{Si}(\text{H})(\text{Me})\text{-O}]_n$ and $[\text{Si}(\text{H})(\text{Me})\text{-CH}_2]_n$ followed by the K_2CO_3 -catalyzed removal of the TMS group in methanol (Scheme 4).⁵⁸ The chemical stability of these polymers was evaluated by dissolving both products in 10%



Scheme 4 Preparation of phenol-grafted PSMs and PSOs ($x = \text{O}$ or CH_2).

$\text{KOH}(\text{aq.})$ and measuring their molecular weight against time.

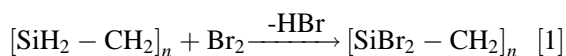
In the case of the polysiloxane, extensive depolymerization was demonstrated by GPC, even during the deprotection step, whereas for the PSM the resulting phenol derivative was found to be soluble in base and stable even after long standing (24h), whereupon it could be precipitated unchanged by addition of acid. This comparison illustrates at least one potential advantage of the polycarbosilane backbone as a substrate for functional polymeric materials relative to the polysiloxanes, where the stability towards hydrolysis in strongly basic or acid media is likely to be considerably better for the PSMs.

4.2 Use of the hyperbranched carbosilane HBPSE as a substrate for polymer modification reactions

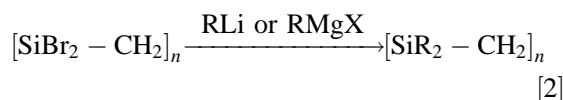
The relatively high cost associated with PSE and the other PSMs obtained by ROP of DSCB monomers constitutes a significant obstacle to the use of these functionalized polymers for most potential applications. In an effort to provide a lower-cost and more versatile substrate for polymer modification reactions that may lead to functional polymeric materials for applications such as battery electrolytes, attention was directed to the modification of the hyper branched polycarbosilane (HBPSE) described earlier in this review. In contrast to the 10–100 g scale on which most DSCB preparations are conducted, the synthesis of HBPSE is routinely carried out on a 500–1000 g scale and has even been conducted successfully on a 6-liter scale by a commercial supplier. It is also currently available as a commercial product. (Starfire Systems, Inc., 877 25th Street, Watervliet, NY, USA.)

Although attempts to use HBPSE itself to hydrosilylate olefins proved unsuccessful, the use of

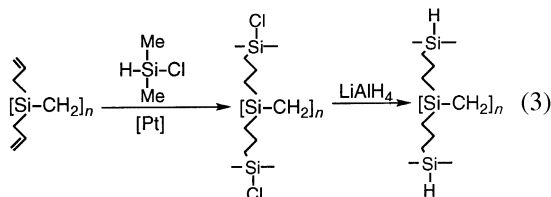
Br_2 in CCl_4 was found to convert a high fraction (>90%) of the Si–H bonds in HBPSE to Si–Br without measurable backbone cleavage, yielding a highly reactive intermediate for polymer modification reactions (Eqn [1]):



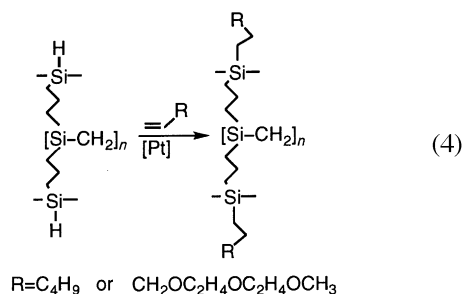
Treatment of this brominated HBPSE with organolithium reagents [RLi; R = n-butyl, n-hexyl, n-octyl, phenyl or $\text{C}_6\text{H}_4\text{N}(\text{Me})_2$] or Grignard reagents (RMgBr ; R = Et, allyl) led to the corresponding alkyl- or aryl-substituted HBPSE to the extent of 70–90% substitution (Eqn 1):



The allyl-substituted HBPSE, which is also accessible directly from the 'chlorocarbosilane' intermediate in the HBPSE synthesis at the *ca* 90% substitution level (Q. Shen and L. V. Iterrante, unpublished work), can be used as a synthetic platform for attaching various functional side-chains via the hydrosilylation reaction. In this case, $\text{Si}(\text{Me})_2(\text{H})(\text{Cl})$ is first added to the allyl groups by hydrosilylation and then the remaining Si–Cl is reduced to Si–H with LiAlH_4 (Eqn [3]):



The resulting silane then hydrosilylates terminal olefins in high yield to give the desired side-chain derivative. In this manner, a polymer which was substituted with *ca* 75% of $-\text{C}_3\text{H}_6\text{Si}(\text{Me})_2\text{C}_3\text{H}_6\text{O}-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{OCH}_3$ side-chains was obtained (Eqn [4]).⁴⁰



This polymer was found to have a low T_g

(-84°C) and to dissolve lithium triflate readily. The ionic conductivity of these prospective ionic electrolyte materials is currently being evaluated.

CONCLUSIONS

Improved synthetic routes to the substituted disilacyclobutanes that are used as monomers in the ring-opening polymerization process employed for the synthesis of PSMs have 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 groups and side-chains on to the polymer backbone. These PSMs constitute a new class of inorganic/organic hybrid polymers that effectively bridge such inorganic polymers as the polysiloxanes, polysilanes and polyphosphazenes with the all-carbon backbone polyolefins. Similarly substituted polymers of these different types (as well as certain of the parent, unsubstituted, polymers) have been examined, yielding important fundamental information relating to the effect of the polymer backbone on such properties as T_g and T_m . In particular, studies of the parent PSM, polysilaethylene, have revealed significant similarities and important differences relative to polyethylene. This includes a similar all-*trans* crystalline structure for the solid form but with a much lower melting transition that appears to relate to lower torsional barriers in PSE due to the longer Si–C backbone bond length. PSE was also studied as a precursor for silicon carbide, leading to information regarding the polymer-to-ceramic conversion process. Polymer grafting reactions analogous to those carried out on the chloro-substituted PSMs have also been applied to a hyper branched version of PSE (HBPSE), providing a relatively low-cost route to functionalized polycarbosilanes.

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