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Syntheses and Studies of Organosilicon Compounds

by

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DEDICATION

TO MY PARENTS

GENERAL INTRODUCTION

The syntheses of polycarbosilanes and polysilanes as silicon carbide ceramic precursors have been active research areas in the Barton Research Group. In this thesis, the work is focused on the preparation of polycarbosilanes and polysilanes as stoichiometric silicon carbide precursor polymers. The syntheses of the precursor polymers are discussed and the conversions of these precursors to silicon carbide via pyrolysis are reported. The XRD pattern and elemental analyses of the resulting silicon carbide ceramics are presented.

Silicon monoxide is an important intermediate in the production of silicon metal. The existence of silicon monoxide in gap phase has been widely accepted. In the second part of this thesis, the generation of gaseous silicon monoxide in four different reactors and the reactions of gaseous silicon monoxide towards organic compounds are discussed.

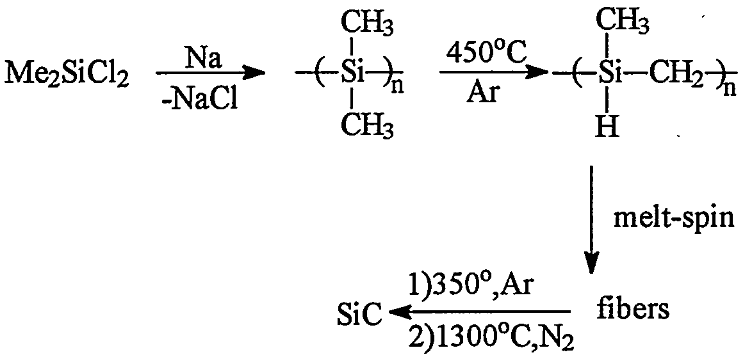
I. THE SYNTHESES OF SILICON CARBIDE PRECURSOR POLYMERS

Literature Survey

Silicon carbide (SiC) ceramic is a promising material because of its exceptional thermal stability and high resistance to oxidation (up to 1400 °C) as well as its mechanical properties. It is also used as a semiconductor, having a wide band gap (2.2-3.0 eV). Due to its excellent performance in high-temperature, high-power, high-frequency and radiation-resistant systems, SiC is particularly useful for electronic applications.[1] To date semiconductor-grade SiC films are fabricated primarily by the use of modern deposition techniques such as chemical vapor deposition (CVD) and laser-induced chemical vapor deposition.[2]

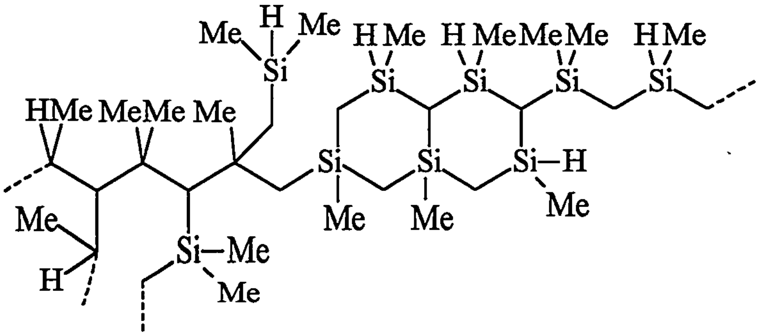
Over the past 20 years intense research has been focused on the syntheses of organosilicon compounds as SiC ceramic precursors.[3-10] The conversion of polymeric precursors such as polycarbosilanes (PCS) and polysilanes (PS) to SiC has drawn more and more attention because ceramic forms such as fibers and films, which are difficult to obtain by conventional powder processing methods, can be prepared from these precursors. The use of polymeric precursors also allows the formation of high- and controlled-purity ceramics. Dunogues et al.[11] have pointed out in their review that an idealized pre-ceramic polymer should possess a compromise of following properties: (1) sufficiently high molecular weight of the precursor polymers to prevent any volatilization of oligomers; (2) polymeric structures containing cages or rings to decrease the elimination of volatile fragments resulting from backbone cleavage and the latent reactivity in the polymers to obtain thermally-induced cross-linking; (3) viscoelastic properties such as fusibility, malleability and solubility to ensure easy processing; and (4) low organic group content to increase ceramic yield and avoid the production of excess free carbon. It is interesting that different substituents and variations in the polymer microstructure will dramatically affect the final ceramic properties.

The research on synthesis of polycarbosilanes as SiC precursor polymers was initiated by Yajima's pioneering work in mid-1970's.[6] The basic transformations in Yajima's route to synthesize β-SiC fibers are shown in Scheme 1.



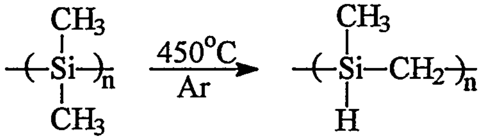
Scheme 1 Synthesis of β-SiC fibers

Heating poly(dimethylsilane) (obtained from Me_2SiCl_2 via Wurtz-type dehalogenative coupling) at atmospheric pressure under argon up to 470 °C resulted in a polycarbosilane with Mn=950 in 35% yield. SiC fibers could be obtained upon pyrolysis under vacuum after air curing. Commercially available PCS known as Mark I, Mark II, and Mark III were prepared by further improvement of the methods mentioned above.[12] From NMR and IR studies, Mark I PCS has a ladder-like structure with rings and branches, as shown in Scheme 2. Yajima also noted that the amount of Si-H in the structure of PCS was crucial to the properties of the resulting SiC fibers. The more Si-H bonds in the precursor PCS, the better properties of SiC. Mark II has a tensile strength of 3 GPa and a Young's modulus of 200 GPa.



Scheme 2 Ladder-like structure of Mark I PCS

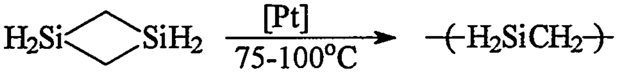
PCS and PS formed by Wurtz-type polymerization Among the synthetic approaches to polysilanes as SiC pre-ceramic polymers, Wurtz-type polymerization of dichloro, trichloro or tetrachloro silanes has been the most extensively investigated so far.[13a] However, the formation of Si-Si or Si-C backbones though this synthetic method rarely tolerates reactive functionalities. Therefore, the polysilanes prepared in this way usually present an intrinsic low latent polymer reactivity that could inhibit further cross-linking reactions during the pyrolysis, which are essential to give a high ceramic yield. These drawbacks are partially overcome by thermal pre-treatment of the precursor polymers. For example, the poly(dimethylsilane) was cured at 430-470 °C to undergo skeletal 'Kumada' rearrangement to form polycarbosilane(PCS) (Scheme3).[13b]



Scheme 3 Thermally induced rearrangement of polydimethylsiane

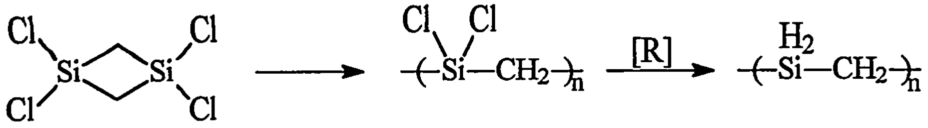
<u>PCS and PS prepared by ring-opening polymerization (ROP)</u> ROP has been proved useful in preparation of stoichiometric precursor polymers for SiC. As already mentioned above, a good precursor for SiC ceramic material should possess 1:1 atomic ratio of Si to C, referred to as stoichiometric polymers, in order to provide a control of the purity in the resulting SiC. Although great challenges exist in syntheses of such materials, a great deal of effort has been spent and a great amount of success has been achieved. Poly(silaethylene) represents the simplest example among the

linear polycarbosilanes having the right Si to C atomic ratio. The preparation of poly(silaethylene) was first claimed by Smith in a patent in 1986. [14] The synthesis of this polymer was accomplished by a ring-opening polymerization (ROP) of disilacyclobutane, using a transition metal catalyst (Scheme 4). They claimed that conversion to SiC ceramic material was achieved in 87% yield. However, no characterization data for this polymer, nor the yield of the ROP reaction was given. The structure of the polymer was doubted by Interrante et al.[15, 16] for their attempts to repeat this ROP synthetic route had resulted in an extremely low conversion of 20% with only 8% yield of hydrocarbon-soluble polymer. Furthermore, the IR and NMR spectra of the polymer indicated branching at Si.



Scheme 4 Ring-opening polymerization of disilacyclobutane [14]

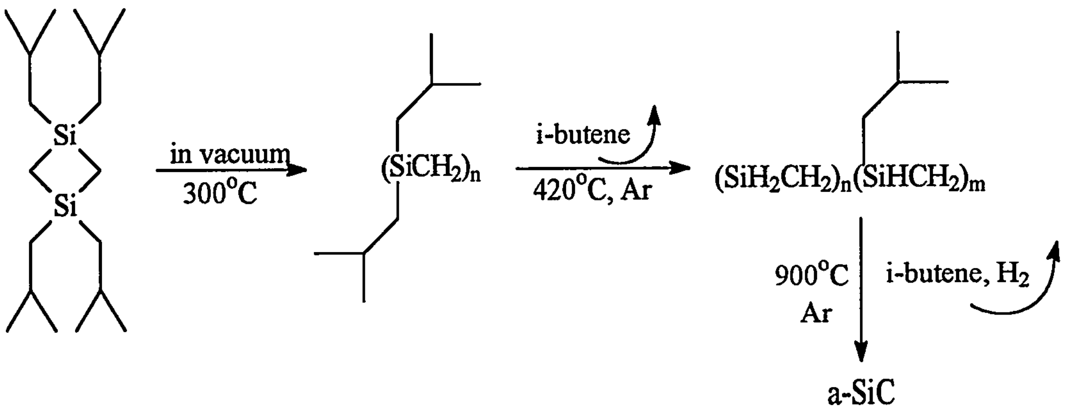
Most of the investigations on ROP to give polycarbosilanes as pre-ceramic polymers have been performed in Interrante's group. Their basic conversion route to form poly(silaethylene) is illustrated in Scheme 5.



Scheme 5 Synthesis of poly(silaethylene)[17]

Poly(dichlorosilaethylene) was prepared by ROP reaction of 1,1,3,3-tetrachloro-1,3-disilacyclobutane catalyzed by chloroplatinic acid or a platinum-divinyltetramethyl-disiloxane complex in benzene.[17] Direct reduction of this product gave the corresponding poly(silaethylene) as a hydrocarbon-soluble, viscous liquid with Mn=12,300, Mw=33,000 vs polystyrene). The ceramic yield from this polymer was 87%. Weight loss started at about 100 °C and stopped after 600 °C. After pyrolysis to 1000 °C in N_2 and holding at that temperature for 1h, the powder X-ray diffraction study of the ceramic product indicated the formation a β-SiC with an average crystallite size of 2.5nm.[18] It was also found that high molecular weight linear polycarbosilanes, when substituted with H on Si, could undergo thermally-induced cross-linking. Thus, the pyrolytic transformation of the hydridopolycarbosilanes to SiC could give a high ceramic yield. The mechanism for this cross-linking process was believed to involve silylene intermediates.[19]

Recently, Fujiuo suggested that a stoichiometric SiC could be obtained from a nonstoichiometric pre-ceramic polymer (Scheme 6).[20] Poly[(diisobutylsilylene)-methylene] was formed by thermal ring-opening polymerization of 1,1,3,3-tetraisobutyl-1,3-disilacyclobutane. DSC studies of this polymer showed that besides



Scheme 6 ROP of 1,1,3,3-tetraisobutyl-1,3-disilacyclobutane and its conversion to α-SiC ceramic material via pyrolysis

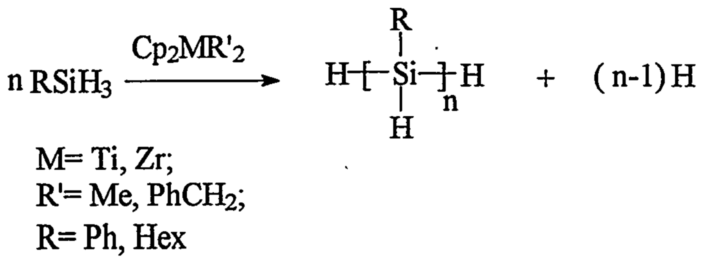
a distinct melting endotherm at 221 °C, a weak exothermic reaction occurred when the temperature reached 265 °C or higher. The IR spectra of both of the volatile products evolved during pyrolysis and the residue recovered after thermal treatment at 420 °C for 15 minutes indicated that the elimination of isobutyl side chains was associated with the formation of Si-H bonds. The composition of the resulting SiC was examined by electron probe microanalysis (EPMA), giving an average composition of the surface region as $SiC_{1.01}O_{0.17}$. Although relatively pure SiC ceramic material was obtained, the ceramic residue yield was only 19%. This low char yield will cause a serious shrinking problem.

PCS and PS formed though Grignard coupling Besides linear PCS and PS, highly branched PCS and PS [21] have also been synthesized as silicon carbide precursors via Grignard coupling reactions. As early as 1964, Kriner noted the formation of some polymeric byproducts when using (chloromethyl)dichloromethylsilane to prepare various cyclic carbosilane compounds.[22] However, no detailed information about these polymeric byproducts was given. In the early 1980's, Schilling et al.[23] studied a number of systems in which various mixtures of Me_3SiCl, Me_2SiCl_2, and $H_2C{=}CHSi(Me)Cl_2$ were treated with potassium, leading to complicated branched polysilanes. Later on, Interrante reported the synthesis and characterization of a novel polycarbosilane with a highly branched structure, whose Si and C ratio is nearly 1:1 (Scheme 6).[24] Chloropolycarbosilane, formed by Grignard coupling reaction, was reduced by $LiAlH_4$ to give the corresponding hydridopolycarbosilane as shown in Scheme 7.

$$Cl_3SiCH_2Cl \xrightarrow[\text{reflux 5 days}]{Mg/Et_2O} \left(Cl_2SiCH_2 \right)_n \xrightarrow[2)H_2O/HCl]{1)LAH} \left(H_2SiCH_2 \right)_n$$

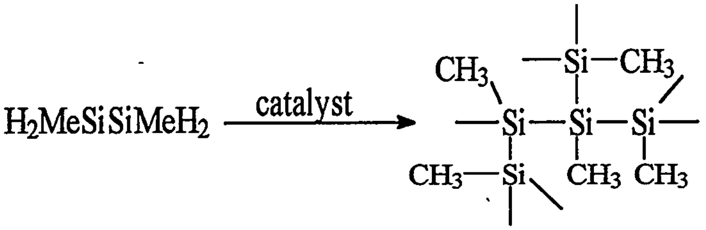
Scheme 7 The preparation of a stoichiometric PCS via Grignard coupling

<ins>PCS and PS synthesized by dehydrogenative coupling</ins> Dehydrogenative coupling is another useful approach to prepare polysilanes and polycarbosilanes.[25] The discovery by Harrod [26] that H functional monosilanes can be linked by formation of Si-Si bonds catalized by transition metal complexes, as outlined in Scheme 8, stimulated the investigation in this area. This synthetic approach offers access to H-containing but low molecular weight polysilanes.



Scheme 8 Formation of polysilane via dehydrogenative coupling

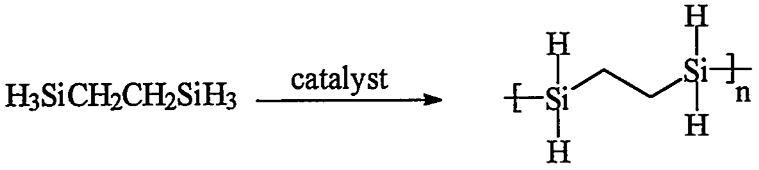
Hengge et al. [27, 28] have widely studied the dehydrogenative polymerization of various substituted disilanes and trisilanes. Among them, the dehydrogenative polymerization of 1,2-dimethyldisilane, using Cp_2MR_2 (M= Ti, Zr; R= Me, n-Bu) as the catalysts, afforded a new unique cross linked poly(methylsilane) with a stoichiometric Si:C ratio, as shown in Scheme 9. Its pyrolysis under Ar at 1500 °C gave a ceramic yield (SiC) of 88%. However, cross-linking took place in the later phase of polymerization, leading to an insoluble and infusible polymer with a general



Scheme 9 Polymerization of 1,2-dimethyldisilane

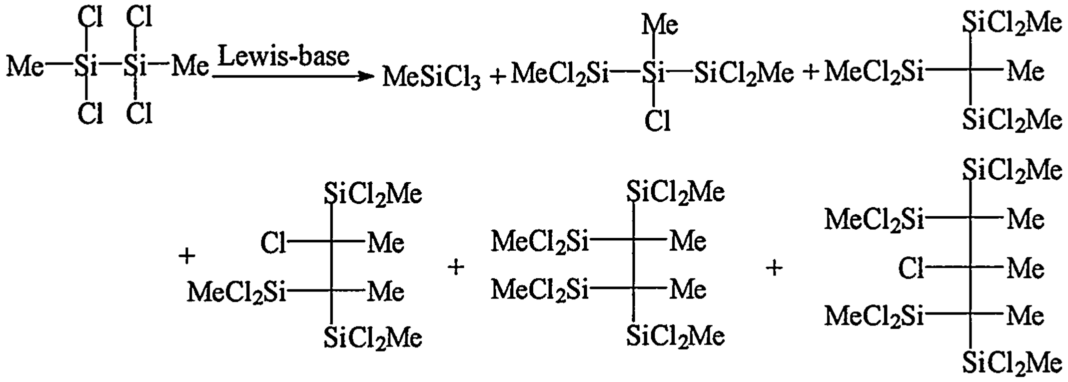
composition of $SiMeH_{0.58}$. Therefore, other than the identification of the oligomers formed at the beginning of the polymerization, no characterization data for the final polymer was given nor was its molecular weight reported in the literature.

Corey and co-workers [29] attempted to use $H_3SiCH_2CH_2SiH_3$ as the monomer to synthesize a SiC pre-ceramic polymer, as shown in Scheme 10, because the Si to C ratios in the monomer and corresponding polymer match that of SiC ceramic. Unfortunately, the polymerization reaction of the 1,2-disilyethylethane with the combination catalyst $Cp_2MCl_2/BuLi$ (M= Ti, Zr) resulted in the formation of a completely insoluble polymer within 30 minutes to 1 hour. Although they tried to slow down the condensation reaction by adding solvent as well as changing to a catalyst system known to decrease rate of dehydrogenative coupling, the direct polymerization of 1,2-disilyethane still gave insoluble materials. Nomura et al. at the Japanese company Tonen Corp., [30] patented the dehydrogenative condensation of a mixture of substituted 1,2-disilyethane(s) and methyl substituted disilane compounds, catalyzed by titanocene. A nitrogen-filled sealed tube was used and a cyclic structure of the copolymer was proposed.



Scheme 10 Polymerization of 1,2-disilyethane

PCS and PS prepared by disproportionation A novel route to the synthesis of poly(chloromethylsilane) via disproportionation of chloromethyldisilanes using *t*-Bu_4PCl as catalyst was first developed by Baney and co-workers at Dow Corning.[31] The polymer synthesized this way was believed to have a high level of cross-linking with average molecular weight of 1000-1300. Spectroscopic identification was unsuccessful due to broad and ill-defined NMR resonance peaks. The basic reaction of catalytic disproportionation of halodisilanes is shown in Scheme 11. This new synthetic route avoids the dehalogenative coupling reaction commonly used to produce PS. Another advantage of this preparation is that it uses a mixture of disilane by-products from the direct process for the synthesis of methylchlorosilanes.



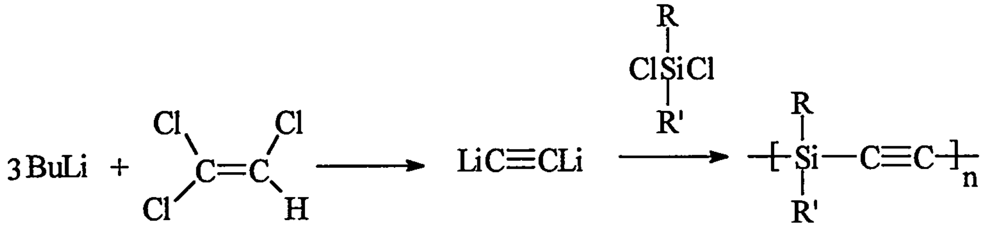
Scheme 11 Disproportionation of dimethyltetrachlorodisilane [31]

Trandell and Urry [32] studied the polymerization of disilane monomers: $MeCl_2Si\text{-}SiCl_2Me$, $MeCl_2Si\text{-}SiCl_3$, and Si_2Cl_6 using trimethylamine as a catalyst.

Oligosilanes such as isotetrasilane and neo-$Si_5Cl_{11}Me_5$ were formed. Richter et al. [33] reported the ^1H, ^{29}Si, ^{13}C NMR and GC-MS identification of the chloromethyloligosilanes formed in the early stages of the disproportionation reaction. They demonstrated that the oligosilane backbones constructed by this method were highly branched and similar to those obtained though dehydrogenative polymerization of 1,2-dimethyldisilane. No linear oligomers nor branched oligomers containing more than 7 Si atoms have been observed. Recently the same group grafted effective catalytic centers such as bis(dimethylamido)phosphoryl, benzimidazolyl or 3,5-dimethylpyrazoly groups onto the surface of silica carriers, using organotrialkoxysilane spacers as graft mediators.[34] Then, the vaporized disilanes were carried in an argon stream to the catalyst bed and the reaction took place on the catalyst surface. In this way, the degree of polymerization can be controlled by removal of the monosilanes and oligosilanes from the reaction system and it is possible to separate the reaction products from the catalyst.

PCS formed via co-condensation of dichlorosilanes with dilithioacetylenes [38-41]

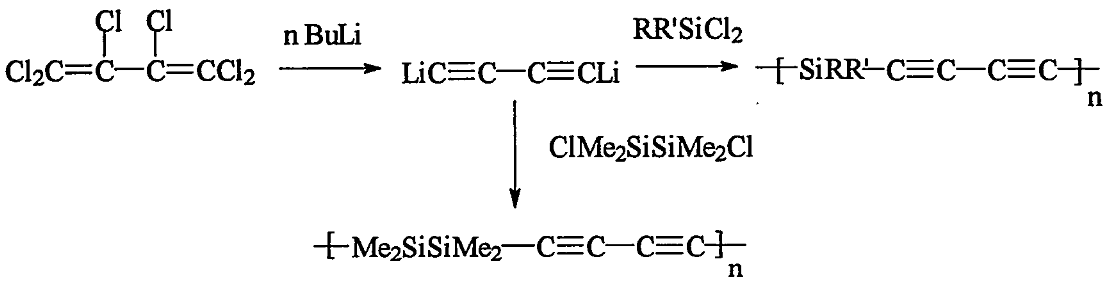
Barton group has obtained polymers with average molecular weights in the range 20,000-30,000 g/mol and TGA residues varying from 20 to 80% (Scheme 12) [39] Melt-spun fibers were thermally or photochemically cured and pyrolyzed to SiC ceramics with various contents of free carbon. Using hexachlorobutadiene as starting material, Barton et al. have synthesized poly(silydiacetylene)s or poly(disilyldiacetylene)s in



Scheme 12 Synthesis of poly(silylacetylene)[40]

good yields (Scheme 13). The TGA data indicated a high ceramic yield (20% weight loss at 1000°C), partly due to a thermally-induced cross-linking, while DSC revealed a strong exothermic peak between 100 and 150°C.

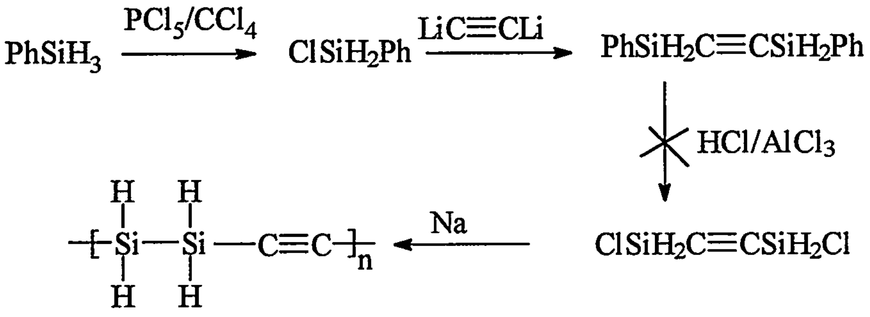
Copolymers of PCS and PS have also been studied. The polymerization of chloromethyldisilanes in the presence of olefins such as styrene, α-methylstyrene, butadiene and isoprene have been investigated by Sartori et al.[35, 36] The copolymers formed in this way, which have rheological properties suitable for fiber spinning,[37] provide promising polymeric precursors for SiC,



Scheme 13 Synthesis of poly(silyldiacetylene)s[41]

Results and Discussion

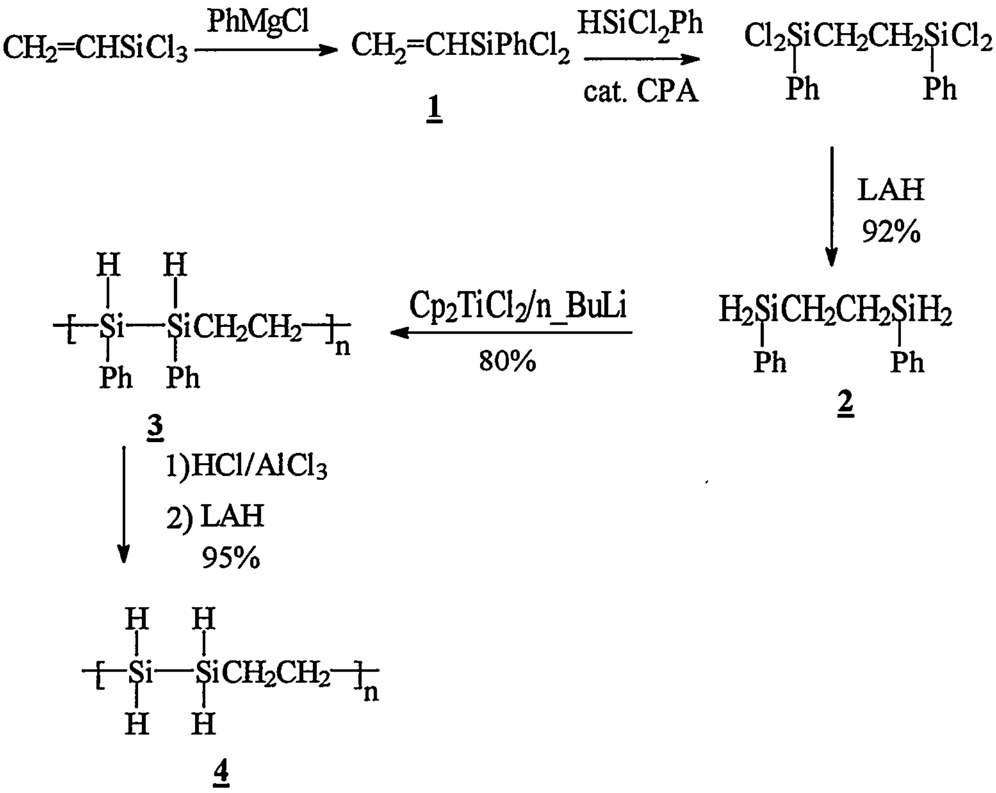
A general search for more efficient polymeric precursors to SiC has been carried out in our group. Zhao [42] attempted to synthesize a silylene-acetylene polymer with small pendant groups. The synthetic approach is depicted in Scheme 14.



Scheme 14 Attempting synthesis of poly(silylene-acetylene)

However, due to difficulties in the synthesis of monomer, $ClSiH_2C{\equiv}CSiH_2Cl$, this route turned out to be unsuccessful. An alternative approach to the synthesis of poly(1,2-disilyethane) failed because of the same problem. This thesis reports the preparation of polycarbosilanes, polysilanes and related copolymers as stoichiometric SiC ceramic precursor polymers.

Synthesis of polycarbosilane 3 and 4 The synthetic route to the formation of polymer $-[SiH_2SiH_2CH_2CH_2]_n-$ 4 is shown in Scheme 15. Dichlorophenylvinylsilane, which was obtained by reaction of trichlorovinylsilane with one equivalent of phenylmagnesium chloride, was reacted with dichlorophenylsilane (1:1 ratio) via hydrosilylation (catalyzed by CPA) to give 1,2-bis(dichlorophenylsilyl)ethane, which was not isolated but reduced with $LiAlH_4$ to afford monomer 1,2-bis(phenylsilyl)ethane 2, in a total yield of 92%. Monomer 2 was polymerized via dehydrogenative coupling, using the combination catalyst, Cp_2TiCl_2/BuLi, to give polymer –$[SiHPhSiHPhCH_2CH_2]_n$- 3 (Mn=1.49E4, Mw=1.54E4) in 80% yield. Polymer 3 contains one phenyl group per repeating unit, which may introduce excess carbon into

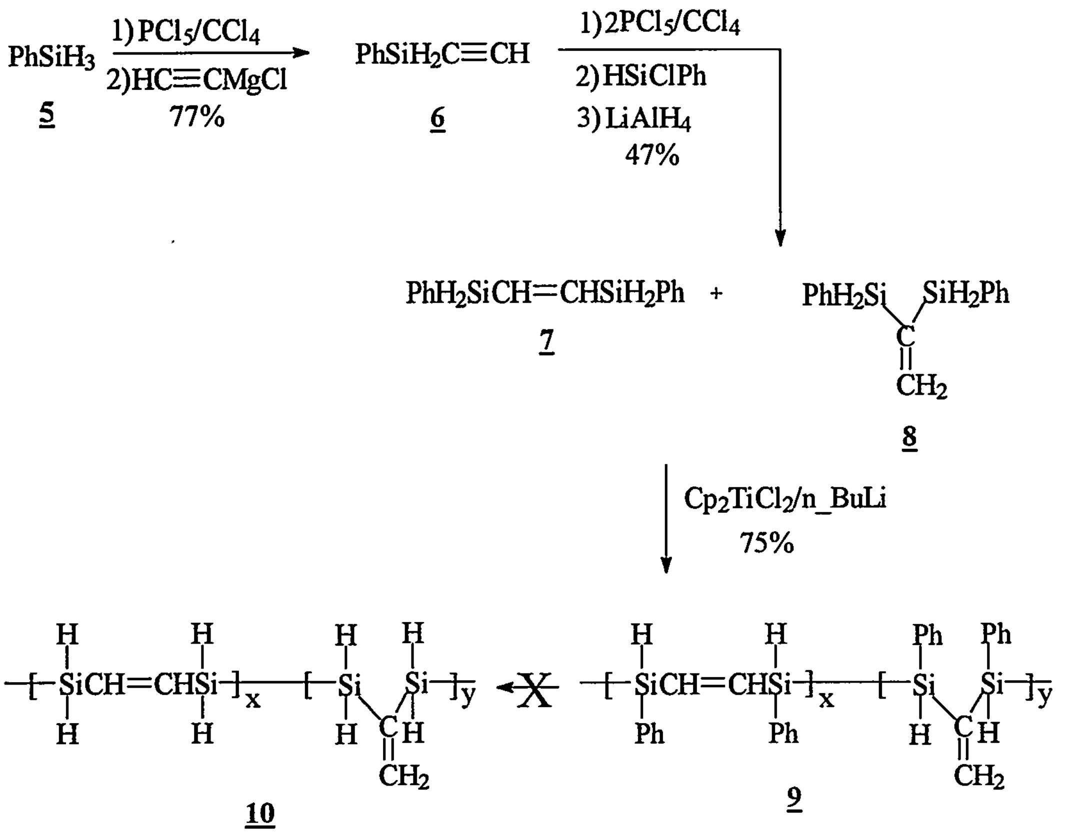


Scheme 15 Synthesis of polymer 3 and 4

the resulting SiC ceramic material and consequently affect its properties. Therefore, polymer 3 is not an ideal precursor polymer for SiC. Therefore, the replacement of the phenyl groups with hydrogen atoms will most efficiently minimize the pendant group and theoretically give the highest ceramic yield upon pyrolysis. This goal was achieved by first replacing the phenyl groups with chlorine atoms via treatment with $HCl/AlCl_3$. The resulting chlorinated polymer could be reduced with $LiAlH_4$, giving polymer 4. The electrophilic cleavage of Si-Ph bond with $HCl/AlCl_3$ was monitored by ^{1}H-NMR spectra. As the reaction proceeds, the decrease of the multiple peaks with chemical shift around 7ppm concede with the growth of a new single peak with chemical shift at 7.4ppm, indicating the cleavage of Si-Ph bond and generation of benzene. After the cleavage of the Si-Ph bond was completed, $LiAlH_4$ was used to reduce the resulting Si-Cl bonds to the desired Si-H bonds. The resulting Polymer–$[SiH_2SiH_2CH_2CH_2]_n$- 4 (Mn=3.15E4, Mw=3.40E4) was still soluble in common organic solvents. According to ^{1}H-NMR integration of polymer 4, the ratio of Si-H to C-H is close to 1, indicating almost exclusive replacement of phenyl groups with hydrogen atoms.

Synthesis of PCS polymer 9 In order to increase ceramic yield, functionalities that afford thermal cross-linking are desired in the precursor polymers. According to previous work of this group, [39-41] the presence of unsaturated bonds such as double and triple bonds should allow for relatively low-temperature cross-linking. Linear silylene-acetylene polymers were converted to SiC via pyrolysis in high ceramic yields with no volatilization of the backbone silicon or acetylenic carbons. It is believed that this behavior of poly(silylene-acetylene) is due to thermal cross-linking as well as the greater bond strength of the silicon-acetylene bond compared to either a silicon-silicon or a silicon-alkyl bond. Therefore, great effort has been spent to make polymers containing unsaturation in the main chain.

The synthetic approach to the preparation of polymer 9 is shown in Scheme 16.

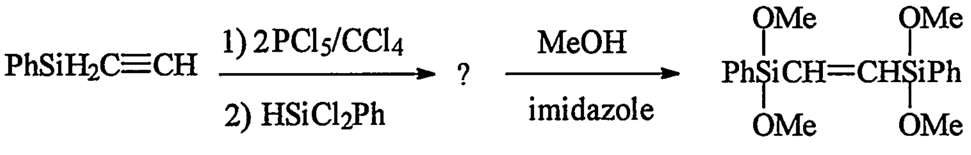


Scheme 16 The synthetic route to polymer 9 and 10

Phenylsilane **5**, prepared from trichlorophenylsilane following a literature procedure [43] but in a greatly improved yield (61% vs 20%), was treated with one equivalent of PCl_5 in CCl_4 at room temperature to afford chlorophenylsilane, which was further reacted with ethylnylmagnesium chloride to give compound **6** in 77% total yield. The formation of bis(dichlorophenylsilyl)ethene by catalytic hydrosilylation of ethylnyldichlorophenyl-silane (obtained by treating compound **6** with two equivalents of PCl_5/CCl_4) with chlorophenylsilane, was established based on GC-MS data. The resulting bis(dichloro-phenylsilyl)ethene was used in next step without further purification to give the monomer **7** and **8** by $LiAlH_4$ reduction.

To our surprise, according to ^{1}H-NMR spectra and GC-MS, both gem- and trans- disubstituted isomers were obtained in a ratio of 1:2. The GC retention times of these two isomers are different by 1.5 minutes. ^{1}H-NMR of compound **8** has a triplet Si-H peak with a chemical shift at 4.60 ppm and a pentlet due to the methene protons with a chemical shift at 6.97 ppm. Whereas the trans-1,2-disubstituted isomer **7**, has two singlets with chemical shifts at 4.63 and 6.68 ppm, assigned to Si-H and =C-H proton respectively. We tried to figure out in which step the two isomers developed. Since the GC-MS spectra of the precursor bis(dichlorophenylsilyl)ethene revealed only one isomer and other instrumental analyses of this compound were not possible due to difficulties in the purification of this compound, a methoxylate derivative, compound **11**, was made by treating the hydrosilylation product with methanol (Scheme 17). GC-

MS analysis only showed a single isomer for compound **11** with m/z=360. This methoxylate derivative was analyzed on a thin layer chomatography (TLC) and only one spot was observed on TLC plate. ^{1}H-NMR spectra also indicated one isomer, in agreement with the GC-MS and TLC results. It is consistent with isomerization during

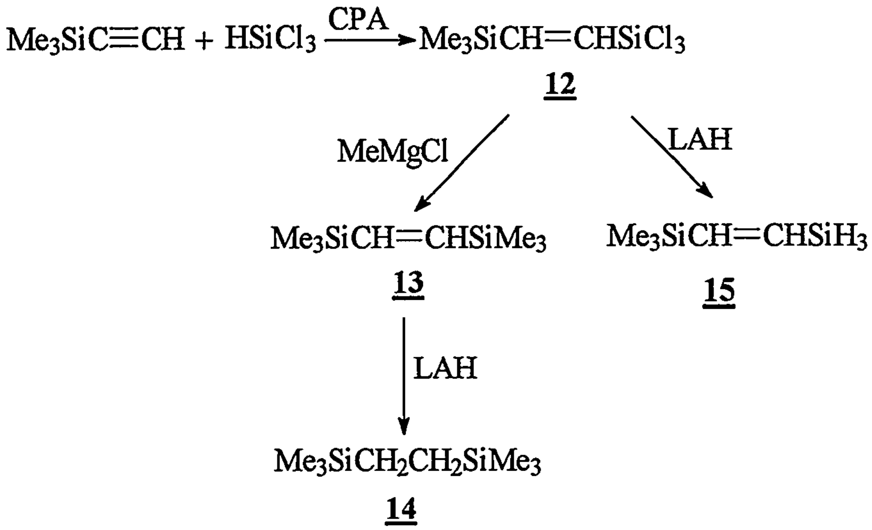


11

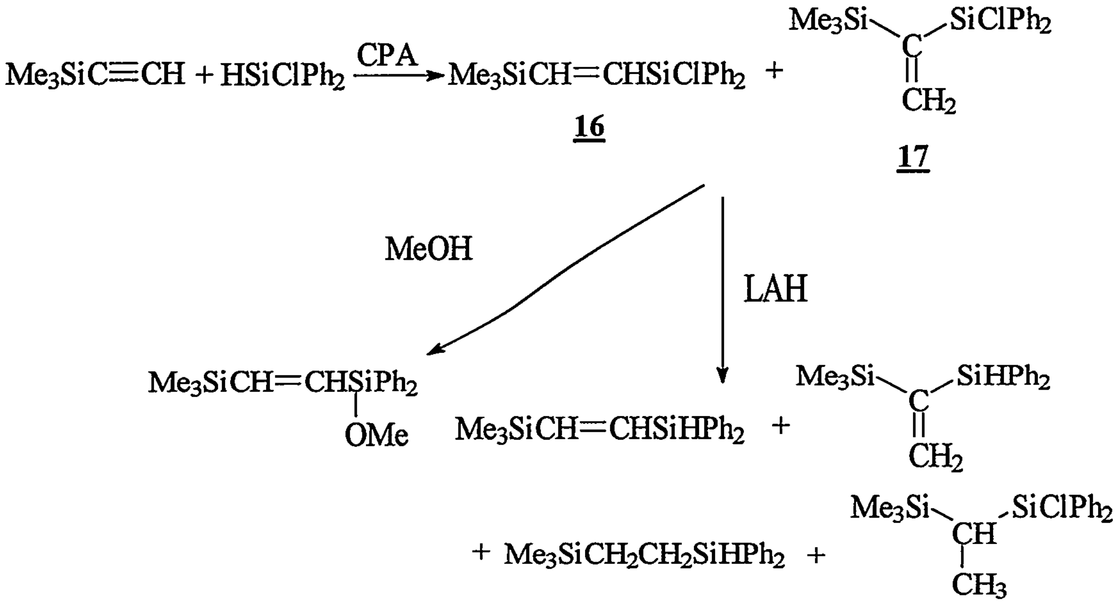
Scheme 17 Synthesis of compound 11

the reduction step instead of during hydrosilylation reaction, which, to our knowledge, is an unknown process.

Therefore, several model compounds were employed in order to find out what was going on. As shown in Scheme 18, the hydrosilylation of trimethylsilylacetylene with trichlorosilane gave compound 12 as a single isomer according to GC-MS, m/z=232. Compound 13 was derived from compound 12 by a Grignard reaction. Both GC-MS and ^{1}H and ^{13}C-NMR indicate only one isomer. Once compound 13 was treated with LAH, compound 14 was obtained. No isomerization occurred during the reduction reaction. Direct reduction of compound 12 gave compound 15, also as a single isomer (proved by GC-MS). This system lacks the phenyl groups on silicon, as in compound 6 . Therefore, a phenyl-containing model system was investigated as shown in Scheme 19. In this case, the hydrosilylation of trimethylsilylacetylene with chlorodiphenylsilane resulted in two isomers, compound 16 and 17, in a ratio of 5:1

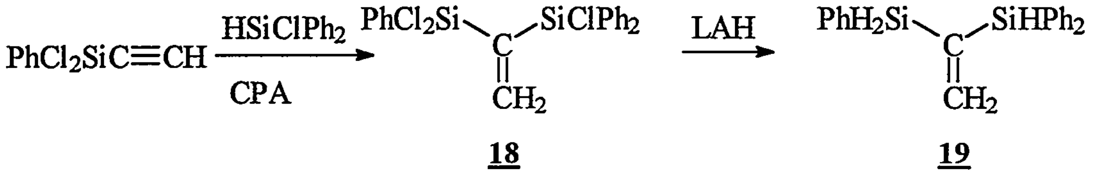


Scheme 18 Synthesis of model compounds 12, 13, 14 and 15



Scheme 19 Investigation of model compound 17 and 18

according to the ^{1}H-NMR integration. However, the GC-MS was not able to resolve these two isomers and the addition of MeOH to the mixture of compounds **16** and **17** gave only a single derivative according to GC-MS. Reducing the mixture of compound **16** and **17** by LAH resulted in the corresponding hydridosilanes with a different ratio (2.7:1). However the change of ratio is not strong evidence for isomerization induced by LAH because the double bond in the starting materials were partially reduced and saturated compounds were detected in the mixture. It is possible that the hydrosilation gives two chlorosilane isomers but the GC-MS can not separate them and the methoxyl derivative favors one isomer over the other. More investigations on the regio-selectivity of hydrosilylation catalyzed by CPA are necessary. One of the experiments carried out towards this end is outlined in Scheme 20. Contrary to our expectations, the hydrosilylation of dichorophenylsilylacetylene



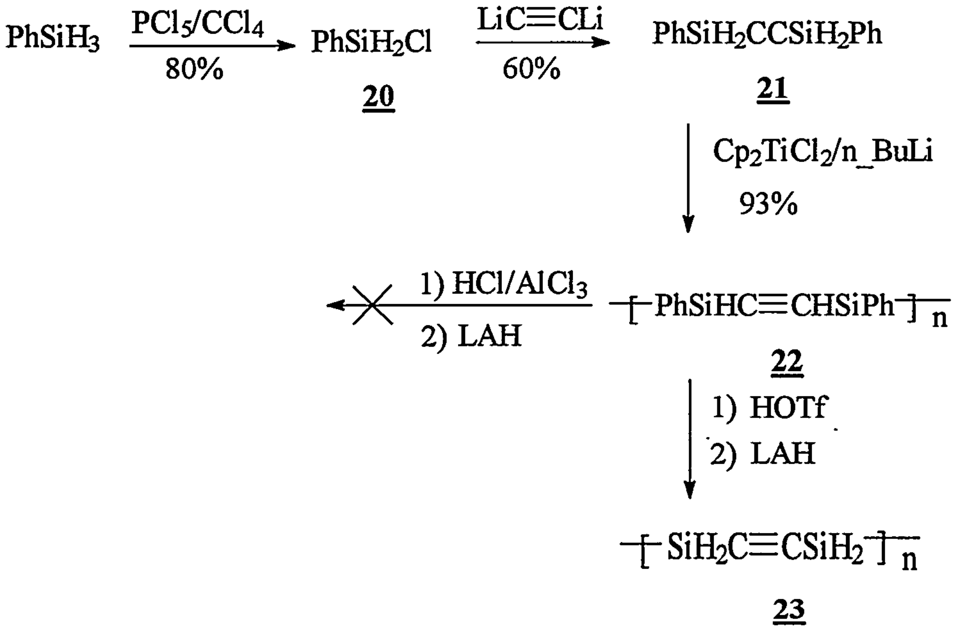
Scheme 20 Hydrosilation of phenyldiclorosilane and reduction of compound **18**

with chlorodiphenylsilane, followed by LAH reduction, gave exclusively compound **19**. The structure of compound **19** was established by ^{1}H-NMR spectra, in which the two different vinyl-hydrogen nuclei coupled to each other with a coupling constant

J=3.3Hz. Although a great deal of effort has been expended, the reason and mechanism for the formation of two isomers were still not clear.

The polymerization of the mixture of monomer 7 and 8 gave polymer 9 in 75% yield.(Scheme 15) The reaction was carried out under similar conditions as in the formation of polymer 4 as described above. However the attempts to produce polymer 10 failed; $HCl/AlCl_3$ not only cleaved the Si-Ph bond but also cleaved the Si-C=C bond readily. Thus, the polymer was cut into small pieces and no precipitate in MeOH was obtained after LAH reduction.

Synthesis of PCS polymer 22 As shown in Scheme 21, monomer 21 was

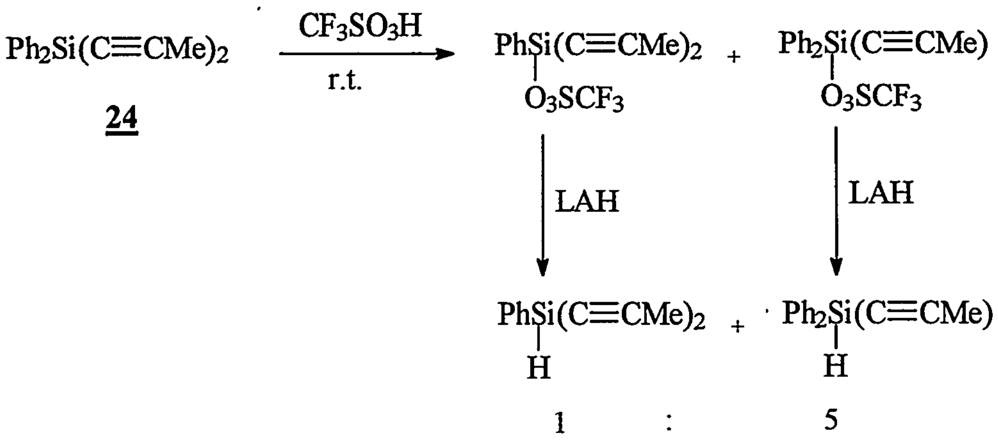


Scheme 21 Synthesis of polymer 22

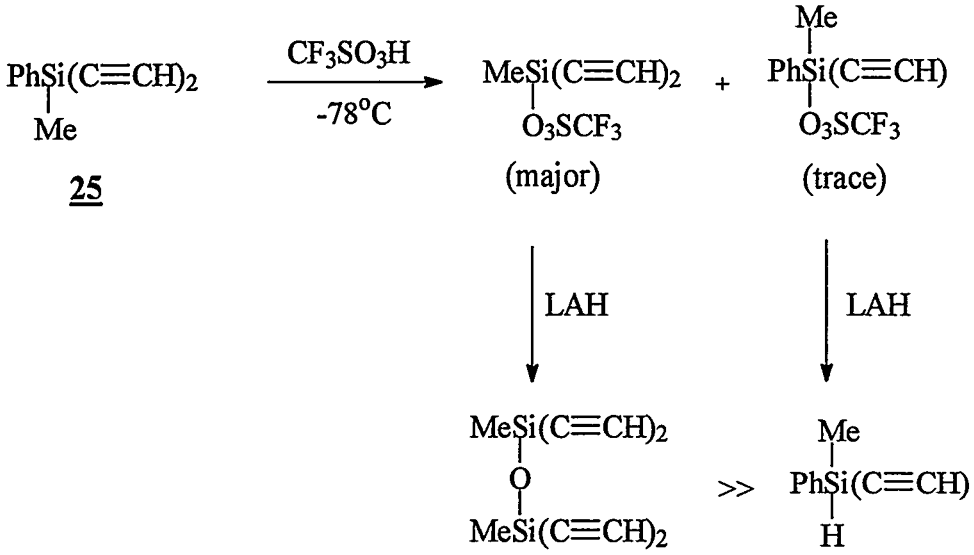
prepared by reaction of chlorophenylsilane with dilithium acetylide, which was quantitatively generated via a reaction of trichloroethylene with thee equivalents of n-BuLi, in an overall yield of 60%. Then monomer **21** was polymerized via dehydrogenative coupling catalyzed by titanocene to give polymer **22** in 93% yield. Considerable effort was spent attempting to convert polymer **22** to polymer **23** by the cleavage of the pendant phenyl groups. Again, the electrophilic cleavage of Si-Ph bond with $HCl/AlCl_3$ failed, as there was no selectivity between Si-Ph bond and Si-C≡C bond under these conditions.

According to literature [44,45], the selective cleavage of Si-Ph bond, while leaving the Si-C≡C bond untouched, can be achieved by using triflic acid instead of HCl and the resulted silotriflate can then be reduced by LAH to give hydridosilane. A study was carried out using model compounds to find the ideal conditions for this reaction. Small molecule $Ph_2Si(C{\equiv}CMe)_2$ **24** was chosen as a model compound and treated with triflic acid at room temperature, followed by $LiAlH_4$ reduction (Scheme 22). GS-MS showed two major products, $PhHSi(C{\equiv}CMe)_2$ and $Ph_2SiH(C{\equiv}CMe)$, in a ratio of 1:5. This ratio means the cleavage of the Si-C≡CMe bond is much easier than that of the Si-Ph bond in this particular compound.

$PhMeSi(C{\equiv}CH)_2$ **25** was also used to investigate this cleavage reaction (Scheme 23). When kept at -78°C, the reaction was incomplete, giving $((HC{\equiv}C)_2MeSi)_2O$ as the major product and a trace $PhMeSiH(C{\equiv}CH)$. However, about equal amounts of $(HC{\equiv}C)_2MeSiOSiMe(C{\equiv}CH)_2$ and $PhMeSiH(C{\equiv}CH)$ were detected when the reaction



Scheme 22 Reaction of trifilic acid with compound 24



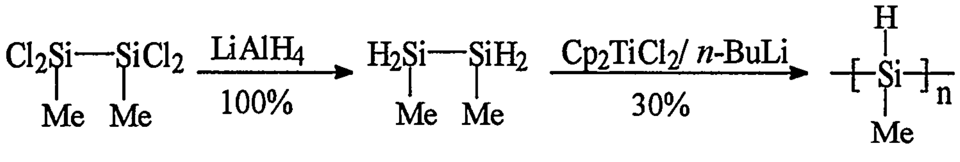
Scheme 23 Reaction of triflic acid with compound 25

mixture was stirred at room temperature for one hour. None of the desired product, MeSiH(C≡CH)$_2$, was observed. The combination of these results indicates: (1) the cleavage of the Si-Ph bond rather than the Si-C≡C is favored at low temperature; (2) the intermediate MeSi(C≡CH)$_2$(OTf) was readily hydrolized to give the corresponding siloxane. Further experiments on this triflic acid cleavage reaction were applied to polymer –[PhMeSi C≡C]- (made in the group). When the reaction was carried out at 40°C, complete cleavage of the Si-Ph bond was confirmed by the ^{1}H-NMR. The broad peaks assigned to the pendant phenyl group, whose chemical shift was around 7 ppm, were replaced with a single peak at 7.4 ppm assigned to benzene. After LiAlH$_4$ reduction, a polymeric material was obtained. Both ^{1}H-NMR and FTIR demonstrated the presence of Si-H bond in the polymer as well as some C≡CH groups.

Finally, the same reaction conditions were applied to polymer **22** in order to remove its phenyl groups. Although the phenyl groups were gone, the resulting material showed no Si-H in ^{1}H-NMR and the C≡C bonds were partially reduced to give saturated C-H with chemical shifts around 1-2ppm. The lack of Si-H may be caused by the hydrolysis of silyltriflates before the reduction with LiAlH$_4$.

Synthesis of polysilane 27- and its copolymers A polysilane, with 1:1 Si to C atomic ratio, has been prepared though a catalytic dehydrogenative polymerization (Scheme 24). Monomer **26** was generated by the reduction of tetrachlorodisilane in quantitative yield. The starting tetrachlorodisilane can be obtained easily from a mixture of several chloromethyldisilanes, which are by-products of industrial 'Direct

Synthesis' of chloromethylmonosilanes, precursors for silicone products. Monomer 26 was distilled out with the solvent (THF) and then the polymerization was carried out in



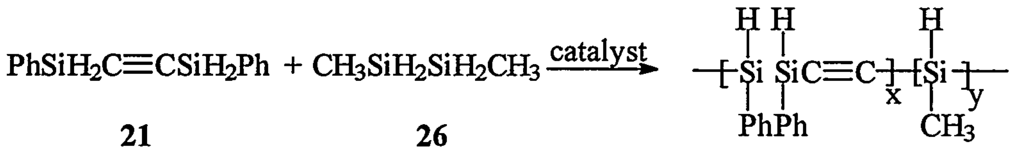
26 27

Scheme 24 Synthesis of polysilane 27

THF. A catalytic amount of Cp_2TiCl_2/2 *n*-BuLi (< 5%) was used to give polymer 27 (Mn=1.25E3 Mw=1.80E3, PDI=1.44) in 30% yield. The number of repeating units was calculated to be 28. The polymer was soluble in common organic solvents but unstable in air. After allowed to sit at room temperature in air for 3 days, an insoluble gel-like material was formed. However, if the polymer was kept in hexane or THF, it was stable for a longer period of time.

In order to improve the spinnability of the polysilane polymers, making them suitable for production of continuous polymer fibers, phenyl groups were introduced into the polymer by copolymerization. Since the rheological models developed for pure organic polymers have to be adapted when applied to organosilicon polymers in many cases, it is difficult to clearly define rules for spinning of organosilane polymers. However, the introduction of phenyl groups is generally believed to improve polymer spinnability.[46, 47]

Copolymer 28 was first prepared for this purpose. (Scheme 25) Only 10% monomer 21 to monomer 26 was utilized, in order to keep a low excess of carbon in copolymer 28. However, in the resulting polymer 28 the ratio of unit -PhHSiC≡CSiHPh- to –HSiMe- changed to 1:2, according to ^{1}H-NMR integration.

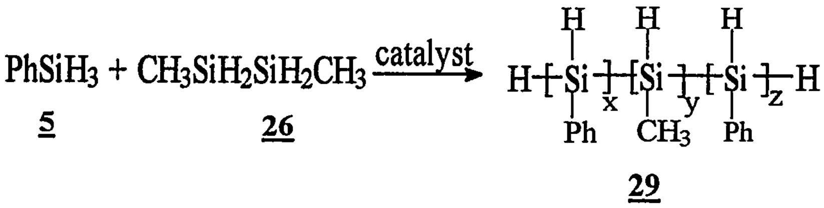


$$PhSiH_2C{\equiv}CSiH_2Ph + CH_3SiH_2SiH_2CH_3 \xrightarrow{catalyst} -\!\left[\overset{H}{\underset{Ph}{Si}}\,\overset{H}{\underset{Ph}{Si}}C{\equiv}C\right]_x\!\left[\overset{H}{\underset{CH_3}{Si}}\right]_y\!-$$

21 26 28

Scheme 25 Synthesis of polymer 28

Then phenylsilane was employed to co-polymerize with monomer 26. Although only 10% phenylsilane was added to monomer 26, the percent of the repeating units containing phenyl groups in the resulting copolymer increased to about 50%. To keep the amount of phenyl groups low, an alternative procedure was applied. At the first stage, only monomer 26 was charged, using catalytic amounts of CPA. After consuming most of monomer 26, phenylsilane was added into the system and the reaction resumed to give a block co-polymer 29 (Mn=3.95E5, Mw=8.79E5). (Scheme 26) In this co-polymer, the feeding ratio of two monomers was maintained according



$$\underset{\underline{5}}{\mathrm{PhSiH_3}} + \underset{\underline{26}}{\mathrm{CH_3SiH_2SiH_2CH_3}} \xrightarrow{\text{catalyst}} \underset{\underline{29}}{\mathrm{H}\!\left[\overset{\mathrm{H}}{\underset{\mathrm{Ph}}{\mathrm{Si}}}\right]_x\!\left[\overset{\mathrm{H}}{\underset{\mathrm{CH_3}}{\mathrm{Si}}}\right]_y\!\left[\overset{\mathrm{H}}{\underset{\mathrm{Ph}}{\mathrm{Si}}}\right]_z\!\mathrm{H}}$$

Scheme 26 Synthesis of polymer 29

to ^{1}H-NMR integration.

Pyrolysis of the precursor polymers The precursor polymers were converted to SiC ceramics via pyrolysis under argon. The general temperature program is: heating at 10°C per minute to 1200°C and isothermal at 1200°C for 1 hour. The ceramic yields were recorded on a TGA. The linear polymer 4, a viscous liquid, had a low char yield of about 15%. The low ceramic yield may be due to the breaking of the polymer main chain before the conversion to SiC. Small volatile molecules generated during pyrolysis were carried out with argon flow. However, the slightly cross-linked polymer 4, which still has excellent solubility in organic solvents, gave a rather high char yield of 45% (Figure 1). Polymer 3, 9 and 22, having pendant phenyl groups, gave higher char yields of 62%, 70% and 85%, respectively (Figure 2, 3, 4). The free carbon contents in the resulting SiC have not been determined, however they are likely to increase with an increase in the C/Si ratio in the starting polymers.

The pyrolysis of polymer 3 and 4 were also monitored on an on-line mass spectrometer connected to a furnace. For polymer 3, the formation of benzene was observed in the MS spectra around 300°C, demonstrating the cleavage of the dependent

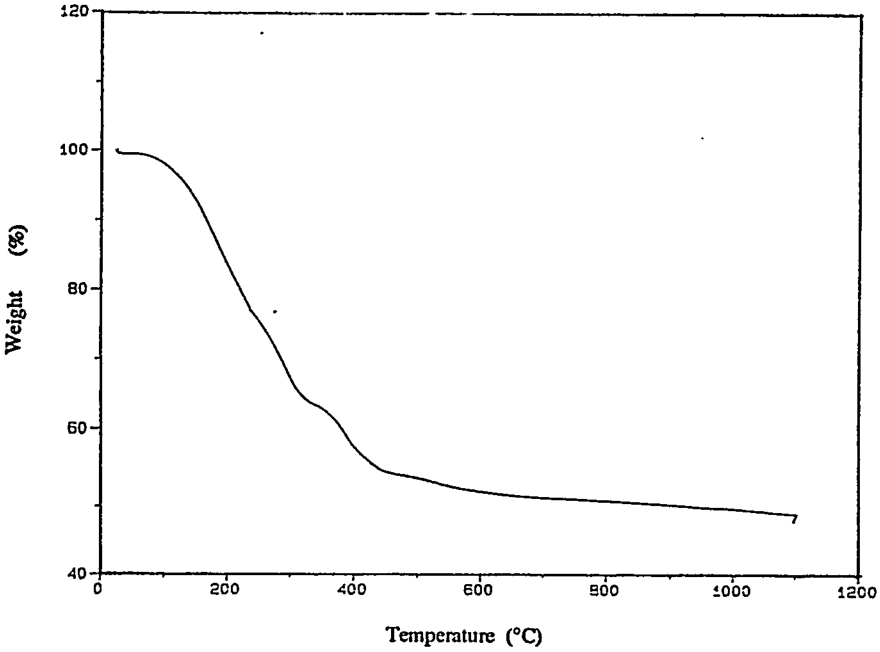


Figure 1 TGA curve for polymer <u>4</u>

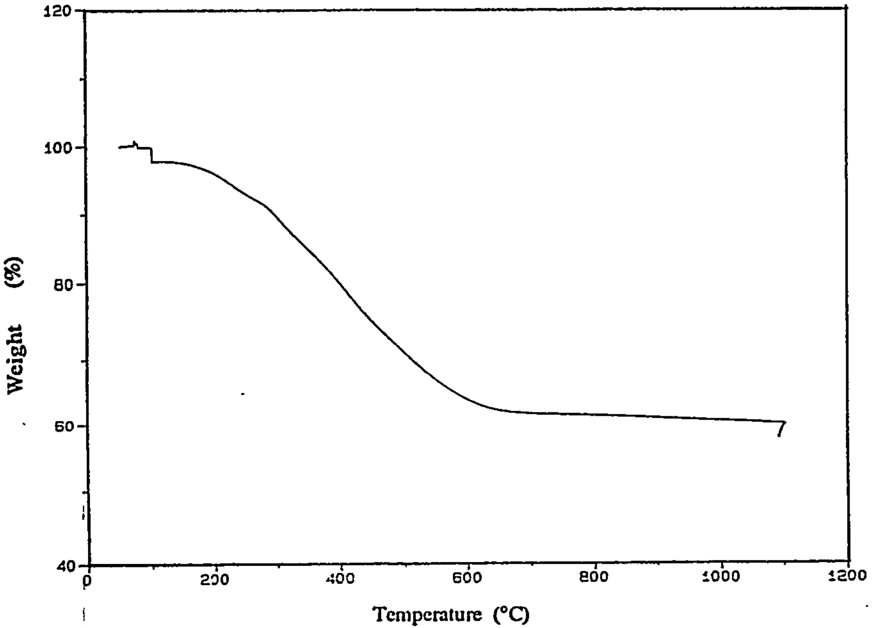


Figure 2 TGA curve for polymer <u>3</u>

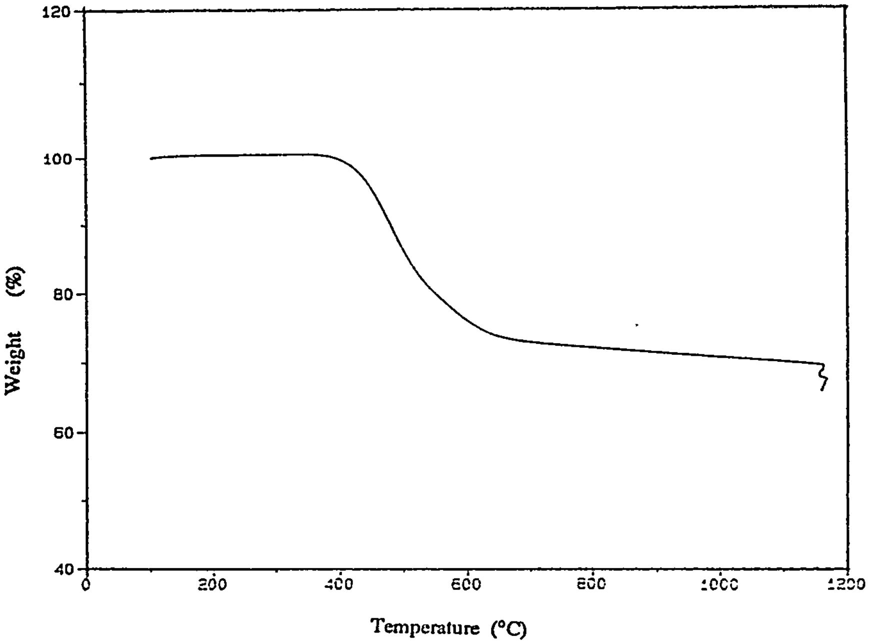


Figure 3 TGA curve for polymer 9

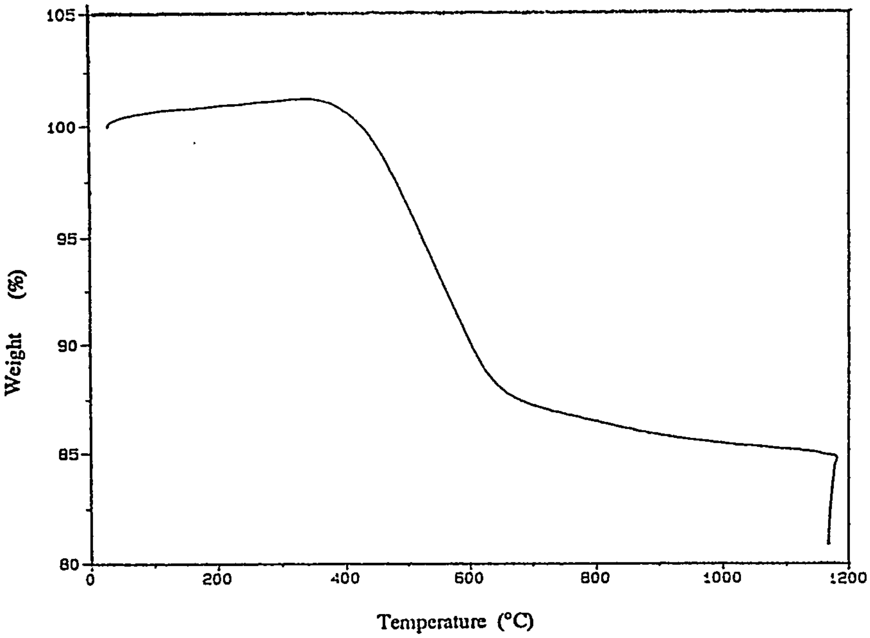


Figure 4 TGA curve for polymer 22

phenyl groups during the pyrolysis. As the temperature approached 500°C, phenylsilane showed up, which means the weight loss at this point also due to the breaking of Si-C bonds in polymer main chain. After 600°C, no further weight loss occurred according to TGA but benzene can still be detected in the on-line MS spectra. The continuous observation of benzene may be caused by the absorption of trace amount of benzene on the walls of the channel connecting the furnace and the mass detector. For polymer <u>4</u>, with only hydrogen atoms attached to Si-C main chain, the weight loss before 200°C was mainly due to the evaporation of solvent (THF) from the polymer. After the temperature rose above 200°C small molecules such as monomer and dimer were detected. Above 400°C the weight remained almost unchanged untill 1100°C (the final temperature of pyrolysis).

The pyrolysis of polymer <u>27</u> without pre-heating gave SiC ceramic in 50% yield (Figure 5). Because polymer <u>27</u> contains large amount of Si-H, which are believed to have latent cross-linking reactivity during pyrolysis[15, 48], its ceramic yield can be improved by curing under argon. Treating polymer 5 at 200°C for 5 hours resulted in 9% weight loss and the formation of an insoluble gel. The gel was pyrophoric in air. Conversion of this gel to SiC ceramic was carried out on TGA, using the same temperature program mentioned above. The char yield was improved dramatically to 88% (Figure 2), which is close to the theoretical ceramic yield for polymer <u>27</u> (91%). The char yield of this polymer after thermal treatment is high enough to avoid any shrinking problems associated with a large weight loss during the

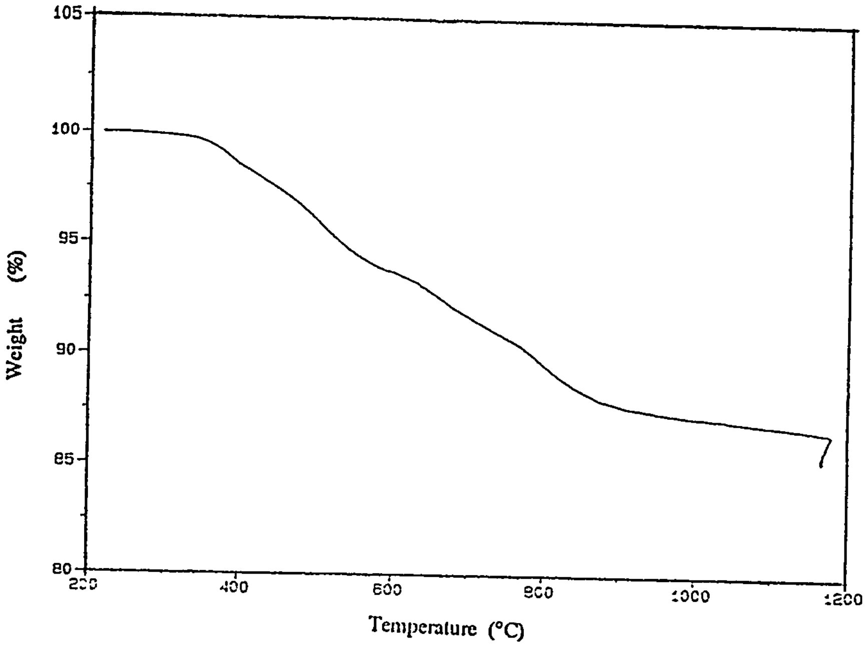


Figure 5 TGA curve for polymer 27

pyrolysis. A processable polymer with latent reactivity during pyrolysis is always desired as a precursor polymer for SiC. The solubility of polymer 27 allows easy processing and the exact 1:1 ratio of Si/C ensures a high purity of the resulting SiC ceramic material. These properties, as well as the practical method of its synthesis, make polymer 27 a very promising candidate as SiC ceramic precursor polymer.

Pyrolysis of the copolymer 29, polymethylsilane terminated with polyphenylsilane, was carried out on TGA, giving 86% char yield (Figure 6).

X-ray powder diffraction (XRD) The XRD spectra of the SiC formed by pyrolysis of polymer 4 was recorded on a SCINTAG XDS-2000 generator (as shown in Figure 7). The 2θ values at 35°, 60° and 72° are consistent with the 2θ values of β-silicon carbide in literature[50]. Because the pyrolysis was carried out at a temperature

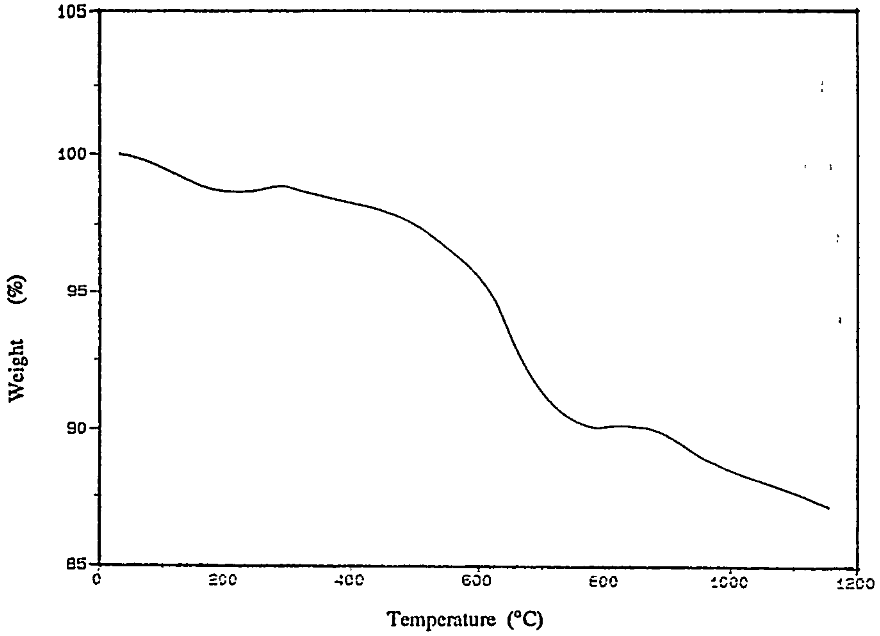


Figure 6 TGA curve for co-polymer 28

lower than 1200°C, the XRD peaks are broad. The average crystallite size of this material, calculated by the line broadening of the XRD pattern, was 2.1nm.[18]

Elemental Analysis of SiC ceramics The PE 2400 CHN/S analyzer was used to analyze SiC ceramics for carbon content. The results are listed in Table 1. The theoretical %C value for SiC is 30.0. Interestingly, the published value for the NIST standard of SiC is 29.43. [88] Due to a lack of true standard, the accuracy of this experiment was about +/- 2%. Polymer 3 and 22, containing phenyl pendent groups, had excess carbon in the material. Stoichiometric precursor polymer 4 contained 26.32% carbon in the material, which is close to the theoretical %C value for SiC. The other stoichiometric precursor polysilane 27 showed a carbon content much lower than the theoretical value. This means an excess of silicon presents in the material,

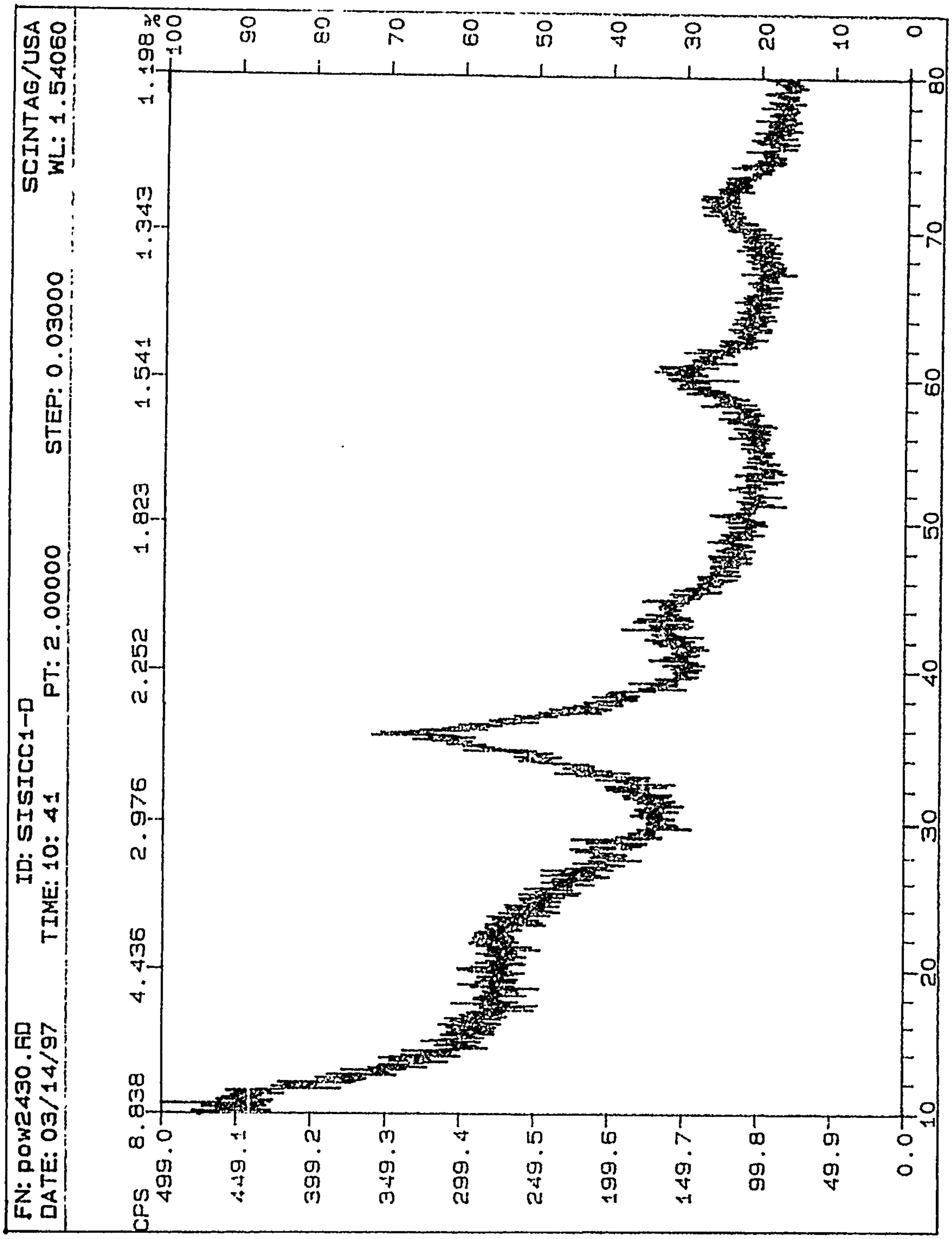


Figure 7 The XRD pattern of SiC from pyrolysis of polymer 4

Table 1 Carbon contents in SiC ceramics from different polymer precursors

Polymer precursors	wt %C in char
Polymer <u>3</u> $-(SiHPhCH_2CH_2SiHPh)_n-$	51.67
Polymer <u>4</u> $-(SiH_2CH_2CH_2SiH)_n-$	26.31
Polymer <u>22</u> $-(SiHPhCH{=}CHSiHPh)_n-$	49.46
Polymer <u>27</u> $-(SiHPhCCSiHPh)_n-$	17.49
Polymer <u>29</u> $-(CH_3SiH)_n-$	18.6

probably due to the cleavage of methyl groups during pyrolysis. Based on these results, a co-polymer of poly(methylsilane) and Poly(phenylsilane) could be converted to SiC with an ideal carbon content as well as desired rheology for production of fibers and films. Actually, copolymer <u>29</u>, did show a 1.2% higher carbon content than polymer <u>27</u>.

Conclusions

We successfully synthesized a series of polycarbosilanes, polysilane and related copolymer as SiC ceramic precursors via dehydrogenative coupling. Among them, polymer <u>4</u> and polymer <u>27</u> have exact 1:1 ratio of Si to C. The polymers were characterized by ^1H and ^{13}C NMR, FTIR , GPC and TGA.

The ceramic yield of each polymer was measured by TGA. Polymer **3**, containing phenyl groups gave higher char yield than its hydridosilane analogue **4**. The presence of unsaturation allowed for higher char yield of polymer **9** and **22**. Polymer **27** and related copolymer **29** can undergo a thermally induced cross-linking during the pyrolysis, thus gave the highest char yield. The elemental analysis indicated that the carbon contents of the SiC ceramics dependent on the structure of the precursor polymers.

Experimental

Reactions were monitored by Hewlett Packard 5890 series II GC and Hewlett Packard GC-MS (5972 series mass selective detector).

Characterization of synthesized compounds was based on MS, IR, ^{1}H and ^{13}C-NMR spectra. ^{1}H and ^{13}C-NMR spectra were acquired on a Varian VXR 300 spectrometer in deuterated chloroform solution. The infrared spectra were recorded on an IBM IR-90 series FTIR spectrometer. The masses were obtained from a Kratos MS 50 mass spectrometer.

Molecular weight of the polymers were determined by gel permeation chomatography (GPC) with 6 Microstyragel columns in series of 500A, 2x10^{3}A, 2x10^{4}A and 10^{5}A. GPC analyses were performed on a Perkin-Elmer series 601LC equipped with Beckman solvent delivery system, a Walter Associate R401 refractive index detector and a Viscotek viscometer. The system was calibrated with polystyrene standards. THF was used as eluent at a flow rate of 1.0mL/min. TGA analyses were performed on a Du Pont model 951 thermal analyzer in Argon atmosphere and 20°C/min. heating-rate unless otherwise specified. The volatile compounds generated during the pyrolysis were monitored by an on-line VG SX300 quadruple mass spectrometer. X-ray powder diffraction spectra were obtained on SCINTAG XDS-2000 generator.

THF was distilled over sodium-benzophenone and ether was distilled over CaH_2 right before use. Other commercially available reagents were used as received from Aldrich or Fisher Chemical Co. without further purification.

1,2-Bis(phenylsilyl)ethane 2 To a round bottom flask, equipped with a magnetic stirring bar and a pressure-equalizing graduated addition funnel, was added vinylphenyldichlorosilane (3.86g, 19mmol) and a catalytic amount of CPA. At room temperature, dichlorophenylsilane (3.50g, 19mmol) was added dropwise into the flask though the addition funnel. After a few drops of dichlorophenylsilane were added, the reaction was initiated by heating with a heat gun for a few seconds (the color suddenly changed to dark brown). The heat gun was removed and the remainder of the dichlorophenylsilane was added. After the completion of the addition, the reaction mixture was heated at approximately 90°C for about 5h. While the reaction mixture was cooled to room temperature, 20mL of THF was added to dissolve the product (almost pure 1,2-bis(phenyldichlorosily)ethane, identified by GC-MS). The solution of 1,2-bis(phenyldichlorosily)ethane in THF was transferred to an addition funnel though a transfer line under argon and then added dropwise to a dispersion of $LiAlH_4$ (1.5g, 39.5mmol) in THF (50mL). After the addition was complete, the mixture was continuously stirred at room temperature over night. The residue was removed by filtration and the solvent was removed with a rotatory evaporator. To the residue, 200mL hexane was added and then washed with water. The organic layer was dried over Na_2SO_4 and the hexane was removed in vacuum. The crude product was purified by distillation at 110°C/0.01 mmHg to give 4.2g pure 1,2-bis(phenylsilyl)-ethane <u>2</u> in 92% yield.(Lit.[42]) **GC-MS** m/z 241 (M-1, 3), 164 (30), 136 (32), 107 (100), 105 (95); **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 1.04-1.05 (s, 4H, $-CH_2$), 4.35 (s, 4H, $-SiH_2$), 7.36-7.60 (m, 10H, phenyl); **^{13}C-NMR** (300MHz, $CDCl_3$) δ(ppm) 4.55 (sp^3, $-CH_2$), 128.06 (sp^2, -CH), 129.75 (sp^2, -CH), 132.33 (sp^2, -C), 135.36 (sp^2, -CH).

Phenylsilane <u>5</u> Following a literature procedure,[43] a solution of $PhSiCl_3$ (42g, 0.198mol) in dry ether (50mL) was added slowly into a slurry of $LiAlH_4$ (3.8g, 0.1mol) in ether (100mL). After the addition was complete, the mixture was refluxed for 5h. The solid was filtered and most of the solvent was distilled off at 30-40°C. Hexane (100mL) was added to the system and water was slowly introduced to consume the excess $LiAlH_4$. The organic layer was washed by water, 2M HCl and water sequentially and dried over Na_2SO_4. After the solvent was distilled, the product was distilled (bp. 120°C) to give 13g of <u>5</u> (Yield 61%). **GC-MS** m/z 108 (M, 98), 107 (100), 106 (95), 105 (70), 78 (10); **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 4.19 (s, 3H, -

SiH_3), 7.41-7.6 (m, 5H, phenyl); **^{13}C-NMR** (300MHz, $CDCl_3$) δ(ppm) 128.23 (sp^2, -CH), 130.69 (sp^2, -C), 133.39 (sp^2, -CH), 134.29 (sp^2, -CH).

Ethynylphenylsilane 6 To a 250mL oven-dried, round bottom flask, equipped with a drying tube (packed with DRIERITE), was charged PCl_5 (15.8g, 76mmol) and dry CCl_4 (100mL). Phenylsilane (8.2g, 76mmol) was poured into the flask. The mixture was stirred at room temperature for 1h and then the solvent (CCl_4) and resulting PCl_3 were removed by distillation. To the residue, was added ethynylmagnium chloride (0.5M, 140mL, 70.4mmmol). Then the mixture was stirred at room temperature over night. The large amount of solvent was removed with a rotatory evaporator and then the residue was extracted by ether. The ether layer was washed twice by water ane dried over Na_2SO_4. Distillation afforded ethynylphenylsilane 6 (Lit.[83]) at about 80°C /3mmHg (7.2g, 54.2mmol, 77% yield). **GC-MS** m/z 132 (M, 59), 131 (100), 105 (57), 77 (16); **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 2.68 (s, 1H, -CH), 4.65 (s, 2H, -SiH_2) 7.44-7.81 (m, 5H, phenyl).

1,2-Bis(phenylsilyl)ethylene 7 To a 250mL oven-dried, round bottom flask, equipped with a drying tube (packed with DRIERITE), was charged PCl_5 (12.5g, 60mmol) and dry CCl_4 (50mL) and cooled in an ice-water bath. Then ethynylphenylsilane 6 (3.9g, 30mmol) was poured into the flask. The reaction took place immediately with the generation of H_2 gas. After stirring at 0°C for 0.5h, the mixture was allowed to warm to room temperature and stirred for one hour and then refluxed for 3h. The solvent

(CCl_4) and resulting PCl_3 were removed by distillation. To the residue (containing mainly ethynylphenyldichlorosilane, checked by GC-MS), was added a catalytic amount of CPA and phenyldichlorosilane (5.3g, 30mmol). Then the mixture was heated at 90°C for 2.5 hs. GC-MS indicated the formation of bis(dichlorosilylphenyl)-ethylene, which was not isolated but reduced by LAH in the next step.

Bis(phenyldichlorosilyl)ethylene (5g, 13mmol) was dissoved in dry THF (10mL) and then added dropwise into a flask which contained an $LiAlH_4$ (0.5g, 13mmol) suspension in THF (10mL) and was cooled in a dry-ice-acetone bath. After the addition was complete, the system was warmed to room temperature. Hexane (100mL) was added into the flask to extract the organic materials. The residue was removed by filtration and the filtrate washed by water, then dried over Na_2SO_4. After the removal of the solvent by a rotatory evaporator, the residue was distilled under reduced pressure (105°C/0.5mmHg) to give a mixture of 1,1-bis(phenylsilyl)ethylene <u>8</u> and trans-1,2-bis(phenylsilyl)ethylene <u>7</u> in a ratio of 1:5. Further purification was carried out on a silica-gel column chomatography to give 0.4g pure 1,2-bis(phenylsilyl)ethylene <u>7</u> (13% total yield). **GC-MS** m/z 240 (M, 5), 209 (23), 183 (40), 162 (100), 147 (17), 131 (23), 107 (29), 105 (46); **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 4.62 (s, 4H, $-SiH_2$), 6.68 (s, 2H, CH) 7.30-7.58 (m, 10H, phenyl); **^{13}C-NMR** (300MHz, $CDCl_3$) δ(ppm) 128.08 (sp^2, -CH), 129.91 (sp^2, -CH), 131.16 (sp^2, -C), 135.58 (sp^2, -CH), 150.05 (sp^2, -CH).

1,2-Bis(dimethoxyphenylsilyl)ethylene <u>9</u> To Ethynyldichlorophenylsilane (4.6g, 23mmol), containing a catalytic amount of CPA, was added dichlorophenylsilane (4.0g, 23mmol). The mixture was heated at 90°C for 2.5h and then poured into a mixture of methanol (10mL) and triethylamine (10mL). After stirring at room temperature for 1 hour, the solvents were removed by rotatory evaporator to give 9 (7g, 85% yield). The product was further purified by PTLC. **GC-MS** m/z 360 (M, 40), 283 (100), 167 (90), 137 (32), 91 (28); **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 3.51 (s, 12H, -OCH_3), 6.72(1, 2H, -CH), 7.33-7.59 (m, 10H, phenyl); **^{13}C-NMR** (300MHz, $CDCl_3$) δ(ppm) 50.81 (sp^3, CH_3), 127.74 (sp^2, CH), 130.08 (sp^2, CH), 132.69 (sp^2, C), 134.90 (sp^2, CH), 151.61 (sp^2, CH).

1,2-bis(trimethylsily)ethylene 13 To $Me_3SiCH=CHSiCl_3$ (3g, 13mmol), was added methylmagnesium chloride (3M, 20mL, 60mmol) though a pressure-equilizing graduated addition funnel. The reaction mixture was stirred overnight at room temperature. After removal of the solvent, the residue was dissolved in water. Hexane (100mL) was used to extract the product from aqueous solution. The organic layer was washed by water and dried over Na_2SO_4. 1,2-bis(trimethylsilyl)ethylene 13 was distilled (bp. 60°C/3mmHg) to give 1.1g in 50% yield. (Lit.[84]) **GC-MS** m/z 172 (M, 8), 157 (30), 99 (10), 73 (100); **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 0.06(s, 18H, $SiCH_3$), 6.58 (s, 2H, CH); **^{13}C-NMR** (300MHz, $CDCl_3$) δ(ppm) –1.57 (sp^3, CH_3), 150.70 (sp^2, CH).

Bis(trimethylsilyl)ethane 14 compound 14 (Lit. [86]) was observed when compound 13 was reduced with excess LAH. Compound 13 (0.5g, 2.9mmol), LAH (0.5g, 13mmol) and 50mL THF were mixed and stirred at room temperature for 24 hs. GC-MS showed a mixture of 14 and 13 in 1:1 ratio. **GC-MS** m/z 174 (M, 10), 159 (20), 131(10), 86 (20), 73 (100); **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) -0.03(s, 18H, $SiCH_3$), 0.36 (s, 2H, CH_2).

Trans-1-(trimethylsilyl)-2-silylethene 15 $Me_3SiCH=CHSiCl_3$ (1g, 4.3mmol) was reduced by LAH (0.5g, 13mmol) at room temperature. After 1h of reaction, compound 15 (Lit. [87] bp. 105-110°C) was detected when was detected by GC-MS. **GC-MS** m/z 130 (M, 5), 115 (90), 99 (95), 73 (100), 59 (70).

1-dichlorophenylsilyl-1-chlorodiphenylsilylethylene 18 dichloroethynylphenylsilane (2.3g, 11.5mmol) was mixed with chlorodiphenylsilane (2.5g, 11.5mmol), followed by addition of catalytic amount of CPA. After stirred at 90°C for 5h, the mixture was checked by GC-MS. The only major product was 18. **GC-MS** m/z 420 (M, 12), 342 (8), 243(15), 217 (100), 181 (25), 165 (20), 77 (10); **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 6.85-6.87 (d, J=3.3Hz, 1H), 7.13-7.15 (d, J=3.3Hz, 1H), 7.15-7.80 (m, 15H). Compound 18 was used as reactant in the next reaction without isolation.

1-diphenylsilyl-1-phenylsilylethylene 19 Compound 18 (1g, 2.5mmol) was added to LAH (0.5g, 13mmol) in 50mL THF at -78°C. After stirring for 1h at -78°C, the solution was warmed to room temperature to give compound 19. **GC-MS** m/z 316 (M, 2), 259 (15), 238(100), 223 (25), 183 (80), 160 (15), 105 (50); **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 4.71 (s, 2H), 5.26 (s, 1H), 6.69-6.70 (d, J=4.8Hz, 1H), 6.82-6.84 (d, J=4.8Hz, 1H), 7.35-7.69 (m, 15H).

Bis(phenylsilyl)acetylene 21 To a 250mL oven-dried, thee-neck round bottom flask, equipped with a magnetic stirring bar and a pressure-equilizing graduated addition funnel, was added 15mL dry THF. The system was flushed with argon and cooled to -78°C (in a dry-ice-isopropanol bath). Then *n*-butyllithium (2.5M, 28.4mL, 71mmol) was introduced at this temperature. Trichloroethylene (2.1mL, 23.6mmol) was added slowly though the addition funnel while efficient stirring was maintained. The addition lasted about 0.5 h (or was slow enough to keep the temperature at -78°C). After the addition, the mixture was stirred at -78°C for an additional 30 minutes and then warmed gradually to room temperature. The mixture was then stirred at room temperature for 1 h. Quite a lot of white precipitate formed during this period of time. Next, the system was cooled to -78°C and phenylchlorosilane (6.72g, 47.3mmol) was added dropwise though the addition funnel. Stirring was continued for one hour at -78°C and then for two hours at room temperature. Ether (50mL) was added to the reaction mixture followed by saturated NH_4Cl solution (100mL). The organic layer was separated and the aqueous layer was extracted with 3 x 50mL portions of ether. The combined organic layer were washed with water, then dried over Na_2SO_4. The solvent was removed with a rotatory evaporation. The resulting crude products (5.0g) was distilled under reduced pressure to give 2.4g (43% yield) of bis(phenylsilyl)acetylene at 110°C/2 mmHg. **GC-MS** m/z 238 (M, 24), 207 (85), 183 (67), 105 (100); **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 4.61 (s, 4H, $-SiH_2$), 7.41-7.6 (m, 10H, phenyl); **^{13}C-NMR** (300MHz, $CDCl_3$) δ(ppm) 109.84 (sp, -C), 128.32 (sp^2, -C), 128.50 (sp^2, -CH), 130.58 (sp^2, -CH), 135.30 (sp^2, -CH); Exact mass m/z 238.06348 (calc. for $C_{14}H_{14}Si_2$ 238.06341)

1,2-dimethyldisilane **<u>26</u>** A solution of 1,2-dimethyltetrachlorosilane (23.5g, 92mmol) in dry THF (50mL) was added slowly to a slurry of $LiAlH_4$ (3.8g, 100mmol) in THF (100mL). After the addition was complete, the mixture was stirred over night. Then the product, 1,2-dimethyldisilane, was distilled out with the solvent in quantitative yield. The yield was calculated based on both NMR and GC-MS data.(Lit.[85] bp. 49°C) **GC-MS** m/z 90 (M, 54), 86 (42), 75 (21), 74 (32), 69 (29), 59 (100); **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 0.18-1.20 (t, 6H, $-CH_3$), 3.48-3.52(q, 4H, $-SiH_2$); **^{13}C-NMR** (300MHz, $CDCl_3$) δ(ppm) –11.43 (sp^3, $-CH_3$).

Polymer **<u>3</u>** Butyl lithium (2.5M, 0.44mL, 1.1mmol) was introduced by a syringe into a 10mL round bottom flask containing Cp_2TiCl_2 (0.125g, 0.5mmol). After a few minutes, monomer, 1,2-bis(phenylsilyl)ethane (2.42g, 10mmol) was added to the flask at room temperature. The generation of gas (H_2) could be observed and the color changed to deep green. After the flask was heated at 90°C for one day, 20mL hexane was added in portions to terminate the polymerization. Then about 10mL of $HCCl_3$ was added and the organic mixture was washed in sequence by water, 2M HCl and water again and dried over Na_2SO_4. After removing the solvents, a sticky oily product (1.94g) was obtained in 80% yield. **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 0.87-1.01 (broad, 2, $-CH_2$), 4.23-4.32(broad, 1, -SiH); 7.18-7.50 (broad, 5, phenyl) **^{13}C-NMR** (300MHz, $CDCl_3$) δ(ppm) 4.66, 128.17, 129.86, 132.45, 135.42; FTIR υ(cm^{-1}) 3024(m), 2917(m), 2145(s), 2118(s), 1493(w), 1452(w), 1061(w), 920(vs); GPC Mn=1.49 E4, Mw=1.54 E4, PDI=1.03.

Polymer 4 To a 150mL oven-dried, thee-neck round bottom flask, equipped with a magnetic stirring bar, was added polymer 1 (0.63g) in 10mL CCl_4 and a catalytic amount of $AlCl_3$. Shortly after the $AlCl_3$ was added, an exothermic reaction took place and generated lots of gas. Dry HCl gas was introduced into the system by a long needle and passed though the reaction mixture for about 40 minutes. The reaction was monitored by NMR. The replacement of the multiplet for the phenyl group in ^{1}H-NMR by a single benzene peak indicated that the reaction was complete. After the solid was filtered out and the solvent was removed, the resulting poly(chlorosilyl)ethane was dissolved in dry THF (10mL) and then added dropwise into a flask containing a $LiAlH_4$ (0.5g, 13mmol) suspension in THF (10mL). The reaction mixture was stirred at room temperature for 5hs and then ether (100mL) was used to extract the organic materials. The residue was removed by filtration and the filtrate was washed by water, and then dried over Na_2SO_4. After removal of the solvent by rotatory evaporation, polymer 4, as a light yellowish oil, (0.23g, yield 95%) was obtained. **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 0.80-0.92 (broad, 2, $-CH_2$), 4.23-4.32 (broad, 2, $-SiH_2$); FTIR υ(cm^{-1}) 3024(vw), 2918(m), 2888(m), 2795(w), 2146(s), 2120 (vs), 1408(m), 920(s); GPC Mn=3.15E4, Mw=3.40E4, PDI=1.08.

Polymer 9 Polymer 9 was made though the similar synthetic approach described in the preparation of polymer 1. Butyl lithium (2.5M, 0.06mL, 0.16mmol), Cp_2TiCl_2 (0.02g, 0.08mmol) and monomers 1.1-bis(phenylsilyl)ethene and 1,2-bis(phenylsily)ethene (0.4g) were used to give polymer 3 (0.3g) in 75% yield. **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 4.21-4.32, 5.04-5.06, 7.22-7.46 (broad peaks); **^{13}C-NMR** (300MHz, $CDCl_3$) δ(ppm) 128.11, 129.83, 132.02, 135.61; GPC Mn=1.23 E4, Mw=1.24 E5, PDI=10.

Polymer 22 Polymer 22 was made though a similar synthetic approach described in synthesis of polymer 1. Butyl lithium (2.5M, 0.05mL, 0.125mmol), Cp_2TiCl_2 (0.015g, 0.063mmol) and monomers 1,2-bis(phenylsily)acetylene (0.3g, 1.26mmol) were used to give polymer 22 (0.28g) in 93% yield. **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 4.3-5.0, 7.2-7.7 (broad peaks); **^{13}C-NMR** (300MHz, $CDCl_3$) δ(ppm) 109.78, 127.75, 129,91, 130.40, 134.05; FTIR υ(cm^{-1}) 2916 (m), 1848 (w), 2144(s), 1428 (m), 1115 (m), 935 (ms); GPC Mn=4.96 E3, Mw=5.03 E3, PDI=1.02.

Polymer 27 Polymer 27 was synthesized though a similar synthetic method described in the synthesis of polymer 3. Butyllithium (2.5M, 0.06mL, 0.15mmol), Cp_2TiCl_2 (0.02g, 0.08mmol) and monomer 1,2-dimethyldisilane 26 (2g, 22mmol) were used to give polymer 5 (0.6g) in 30% yield. **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 0.24-0.31, 3.61-3.67 (broad peaks); FTIR υ(cm^{-1}) 2960 (m), 2895 (w), 2110 (s), 1409 (w), 1250 (m) 1052 (s) 866 (s); GPC Mn=1.25 E3, Mw=1.80 E3, PDI=1.44.

Co-polymer 29 To a mixture of BuLi (2.5M, 0.09mL, 0.22mmol) and Cp_2TiCl_2 (0.025g, 0.1mmol), was added monomer 26 (2g, 22mmol). The solution was stirred at room temperature for 2hs before phenylsilane 5 (0.2g, 1.85mmol) was added. When GC-MS indicated no monomer presented, the solution was worked up, using the same procedure described in the synthesis of polymer 3, to give copolymer 29 (1g, 45% yield) **^{1}H-NMR** (300MHz, $CDCl_3$) δ(ppm) 0.07-0.31(broad peak 3.8), 3.68 (s, 1.0), 7.20-7.52(m, 1.0), (according to ^{1}H NMR integration, 17% silicon atoms had phenyl pendent groups.) ; **GPC** Mn=3.95 E5, Mw=8.79 E5, PDI=2.22.

II. STUDIES ON SILICON MONOXIDE

Literature Survey

Theoretically, silicon, like carbon, should have a monoxide as well as a dioxide, but in the case of silicon only the dioxide has been recognized for hundreds of years. The existence of silicon monoxide (SiO) was first reported by Potter in 1907.[51] Since then SiO has drawn considerable attention. It is volatile at temperatures above 1100°C and can be readily vacuum deposited to form amorphous films with small grain size, high dielectric strength and good adhesion to glass. This kind of thin film has wide applications: electrically insulating layers, capacitor dielectrics, optical films, protective overcoats for front surface mirrors and microcircuits, intermediate layers to increase the adhesion of other materials, and as a buffer layer to reduce chemical interactions between other materials.[52a] York studied the reproducibility of the relative composition of SiO films by measuring the absorption coefficient and transmission.[52b] The optical properties of the films are reproducible by controlling the evaporation rate and partial pressure of oxygen. However, the reproducibility of optical properties does not ensure reproducible electrical properties. Besides the applications in optical and electrical devices, SiO also acts as an important intermediate in the production of silicon metal and various grades of ferrosilicon in submerged-arc furnaces by the reduction of high-purity quartz. Filsinger et al.[53] have given a detailed discussion of the role of SiO in the reactions involved in ferrosilicon and silicon submerged-arc furnaces. They believed that silica was not reduced directly to silicon but instead through a silicon monoxide intermediate. A series of reactions involved in this process are shown in Scheme 27.

$$SiO_2 + 3C \longrightarrow SiC + 2CO \qquad (1)$$

$$2SiO_2 + SiC \longrightarrow 3SiO + CO \qquad (2)$$

$$SiO + 2C \longrightarrow SiC + CO \qquad (3)$$

$$SiO + SiC \longrightarrow 2Si + CO \qquad (4)$$

Scheme 27 The reactions involved in the transformation of SiO_2 to Si

The importance of SiO in steel making was presented by Zapffe and Sims.[54] They classified the significant reactions into two groups: (1) those in which SiO_2 is reduced to SiO by the other components in the system Fe-Si-O-H (Scheme 28), and (2) those in which Si reduces the other dissolved oxides to form SiO (Scheme 29).

$$SiO_2 + Fe \longrightarrow SiO + FeO$$

$$iO_2 + H_2 \longrightarrow SiO + H_2O$$

$$SiO_2 + Si \longrightarrow 2SiO$$

Scheme 28 The formation of SiO via reduction of SiO_2 in steel making process

The thermodynamic studies of the first group of reactions signified that with increasing temperature SiO_2 transformed more readily to SiO. This is consistent with the recognition of silicon monoxide as a high temperature form. Whereas in the second group of reactions, the ability of Si to reduce FeO decreased with the increase of temperature, which means the silicon oxides become less stable at higher temperatures in contact with iron. However, the determination of the actual concentration of SiO in liquid steel was incomplete.

$$Si + FeO \longrightarrow SiO + Fe$$

$$Si + H_2O \longrightarrow SiO + H_2$$

Scheme 29 The formation of SiO via oxidation of Si in steel making process

SiO powder is also used to prepare SiC powder. This route to the manufacture of silicon carbide powder was patented by Satoshi et al.[55] SiO powder and C black (mole ratio 1:1) was mixed with 15 wt. % SiC powder and heated under argon at 1700°C. The yield of SiC powder was 95% with average diameter of 0.6 μm.

Silica is the general source of SiO. The attempt to produce SiO by reducing silica with silicon metal (shown in scheme 30) was first tried by C. Winkler.[56] Their experiment failed

$$SiO_2 + Si \longrightarrow 2SiO$$

Scheme 30 The reaction of silica with silicon metal to give SiO

because the maximum temperature did not exceed 1000°C in the combustion furnace. Later the same reaction was performed by Potter [1] in an electric furnace at a temperature higher than 1500°C. When the reaction was carried out in an inert atmosphere, a soft brown, very fine deposit was collected. The percent content of Si in the resulting deposit showed little or no influence due to any change in weight fraction of the starting materials. Therefore, the possibility of parallel distillations from the granular mixture to give the deposit was ruled out. To date, the reduction of SiO_2 with silicon is still the most widely investigated reaction for the preparation of SiO. The thermodynamic data of this reaction were measured by Schafer and Hornle.[57] As mentioned above, the reduction of silica by silicon carbide or carbon is another way to produce SiO which is involved in the industrial production of silicon metal. (Scheme 25) In 1949, Grube and Speidel [58] studied the reduction of silica by hydrogen gas to form SiO by a flow method in an alumina tube between 1473 and 1773K. (Scheme 31)

$$SiO_2 + H_2 \longrightarrow SiO + H_2O$$

Scheme 31 Reduction of SiO_2 by hydrogen gas

Later on, Brewer and Mastick [59] investigated the high temperature decomposition of SiO_2 using an effusion method (Scheme 32).

$$2SiO_2 \longrightarrow 2\,SiO + O_2$$

Scheme 32 Decomposition of SiO_2

The existence of gaseous SiO has been established unequivocally by spectroscopic investigation as early as 1930's. The ultraviolet band system of SiO has heads, as listed by Jevons, [60] extending from 217.7nm to 292.5nm. Cameron [61] and Saper [62] analyzed these bands. Each band was found to consist of one P, one Q and one R branch. Anderson [63] and Hastie [64] reported the investigations of the IR spectra of matrix-isolated SiO species almost at the same time. All of the spectroscopic data supports the existence of single molecular SiO in gas phase.

The existence and structure of SiO in the solid state has raised more controversy. Tone [65] and Winkler [66] could only obtain a mixture of Si and SiO_2 by quenching SiO vapor, but Potter [1, 67] claimed to be able to prepare SiO(s) by suitable quenching. It was widely accepted that if the quenching of SiO vapor is not rapid enough, the mixture of Si and SiO_2 will result due to the disproportionation shown below. (Scheme 33)

Various physical appearances of SiO solid have been reported.[68] Many indications lead one to assume that the color of pure SiO solid and a mixture of Si and

$$2SiO \longrightarrow SiO_2 + Si$$

Scheme 33 Disproportion of SiO

SiO_2 falls in a range of light brown to black.

Hoch and Johnston [69] claimed the observation of SiO from X-ray diffraction patterns taken at 1250°C and 1300°C during various time intervals. The disappearance of the Si diffraction lines and the appearance of a new set of diffraction lines at 1300°C, together with the disappearance of this new set of lines and the reappearance of Si lines upon cooling the sample to room temperature, constituted proof of the formation of solid SiO and its disproportionation to Si and SiO_2 upon cooling. The crystal structure of SiO was found to be cubic with the lattice constants at 1300°C and 25°C being 7.135 and 7.09 Å, respectively. However, this result was doubted by Geller and Thurmond. [70] They thought that Hoch and Johnston only obtained a mixture of β-cristobalite and β-SiC. The conversion of vitreous silica to cristobalite at 1300°C was probably catalyzed by the presence of highly active and finely divided carbon which was present as a result of the degradation and cracking of the organic polymer used as a cement for holding their X-ray samples together. Further X-ray studies were carried out by Brady. [71] They believed that the material described as "amorphous SiO" was a stoichiometric mixture of SiO_2 and Si, according to the Fourier analyses of the scattered intensities.

Despite several investigations, the structure of SiO is not well understood. Two models, random bond model (RB) and random mixture model (RM), are supported by different experimental results. In 1972, Philipp [72] first suggested a RB model to explain his optical reflectance data of SiO films, assuming that Si-Si and Si-O bonds are statistically randomly distributed throughout the SiO structure. This model was supported by both Engelke et al. [73] and Ching.[74] The RM model was first proposed by Temkin [75] and was supported by Etherington et al., [76] based on the neutron scattering investigation of commercially prepared powder samples of SiO. In 1984, Dupree and co-worker [77] used Magic-angle spinning (MAS) NMR to assess the applicability of different structural models to powder samples of amorphous SiO. The spectra indicated that the samples consist of a microscopic mixture of regions of Si and SiO_2 together with a significant amount of interphase material. This result was in best agreement with the quasi-periodic RM model.

Schnockel and co-worker [78] examined the structure of dimeric SiO by matrix infrared investigation and ab initio calculations. The SiO solid was prepared by deposition of gaseous SiO, generated by the reaction of Si with O_2 at a temperature of about 1500°C, with an excess of Ar on a liquid helium-cooled surface. This method has an important advantage in that the concentration of SiO can be varied over a wide range in a highly reproducible way. In the IR spectrum, along with the absorption of monomeric SiO at 1226 cm^{-1}, additional bands attributed to the dimer (803 & 768 cm^{-1}) and the trimer (972 cm^{-1}) were observed. The dimerization of SiO in the matrix depended primarily on the SiO concentration. The ab initio calculation showed that $(SiO)_2$ was remarkably stable, which agreed with their experimental results.

To date the reactivity of SiO is not well known due to its inertness at room temperature. The interaction of SiO, as a CO analogue, with silver atoms was examined first by Mehner et al.[79], using FTIR spectroscopy to show the formation of Ag(SiO), $Ag_2(SiO)$ and $Ag(SiO)_2$. The reaction was carried out in an argon matrix at 10K. Later Chenier et al.,[82] utilizing electron paramagnetic resonance (EPR) spectra, studied this reaction in an admantane matrix at 77K in a rotating cryostat. The EPR parameters showed that in $Ag(Si_2O_2)$ and $Ag(Si_3O_3)$ the silver atom could be η_4- and η_6-coordinated beneath the planar cyclic silicon oxygen frame work.

The interaction of silicon monoxide gas with carbonaceous reducing agents was investigated by Paull and co-worker.[80] SiO gas was generated by the heating of a mixture of silica and silicon carbide, and the progress of the reaction was followed by monitoring the carbon monoxide in the off-gas with an infrared spectrometer. Among the reducing agents (charcoal, Iscor coke, Lurgi char, and petroleum coke), Lurgi char appeared to be the most suitable agent for the production of ferrosilicon because it has a high reactivity towards silicon monoxide gas and high strength when converted to silicon carbide.

Also, SiO can be used as a reducing agent to reduce many metal oxides. Kozhevnikov [81] reported in a patent the behaviour of gaseous SiO during the silicothermic reduction of chromium oxides. The reactions for the formation of SiO in this experiment are shown in Scheme 34. The reduction of chromium oxides at temperatures above 1427°C by SiO took preference over the reduction by silicon metal.

$$Cr_2O_3 + Si \longrightarrow 2\,CrO + SiO$$

$$CrO + Si \longrightarrow Cr + SiO$$

$$Cr_2O_3 + Si \longrightarrow 2\,Cr + SiO$$

$$Cr_2O_3 + 3\,SiO \longrightarrow 2\,Cr + 3\,SiO_2$$

$$CrO + SiO \longrightarrow Cr + SiO_2$$

$$Cr_2O_3 + SiO \longrightarrow 2\,CrO + SiO_2$$

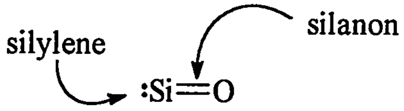
Scheme 34 SiO involved in the reduction of chromium oxide

To date, the research on the reactivity of SiO is very limited.

Results and Discussions

Although the existence of silicon monoxide has been widely accepted, the reactivity of this compound towards other organic compounds is still unknown. SiO has two possible centers of reactivity, as illustrated in Scheme 35. One is the silicon-oxygen double bond or silanone part, the other is the lone pair of electrons or silylene part.

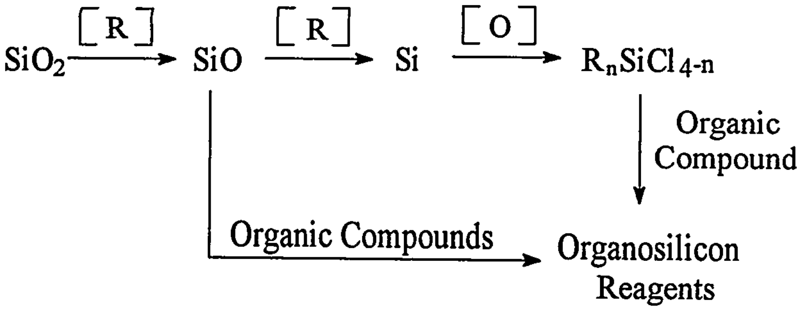
Does SiO have a reactivity similar to its carbon analogue CO? Or does it have totally different reactions with other organic compounds. There are no experimental results to answer these questions. The difficulties for these experiments lie in the fact that SiO tends to disproportionate to silica and silicon metal or to form a random bonded inert network at a temperature reasonable for common organic reactions. Since SiO can exist as a single molecule when extremely diluted, it might be able to be trapped by organic compound. If the trapping reaction succeeds, the nature of SiO can be better understood.



Scheme 35 Possible reaction centers in SiO

On the other hand, the conversion of SiO to organosilicon compounds could be a remarkable revolution in silicon industry. Organosilicon compounds such as chlorosilanes are important precursors to silicone materials and valuable protecting reagents in organic synthesis. The traditional method to synthesize these organosilanes is shown in Scheme 36.

As we can see, the reduction of SiO followed by oxidation of Si metal to give chlorosilanes and corresponding organosilicon reagents is tedious and energy consuming. If SiO can directly react with organic compounds to give organosilicon



Scheme 36 Routes to make organosilicon reagents

reagents, it will save a great deal of energy as well as avoid environmental pollution caused by the reduction and oxidation steps involved in the traditional silicon industries. My research in this project has been focused on the generation of highly diluted SiO and the investigation of its reaction with various organic compounds.

The generation and reaction of SiO in a high vacuum reactor The vacuum reactor (Figure 8) consists of a heated zone section in which the substrate under investigation is pyrolyzed and a pumping section which creates the vacuum. A SiO evaporation vessel (Figure 9) containing commercially available SiO powder was heated with low voltage high current DC power via high current electrical feed-throughs.

A thermocouple was inserted into the empty evaporation vessel and the equilibrium temperature in the vessel at different currents was measured under three conditions: vacuum at $3x10^{-5}$torr, in argon at $5x10^{-3}$torr, and in argon at atmospheric pressure. The calibration lines were shown in Figure 10. The temperatures of other

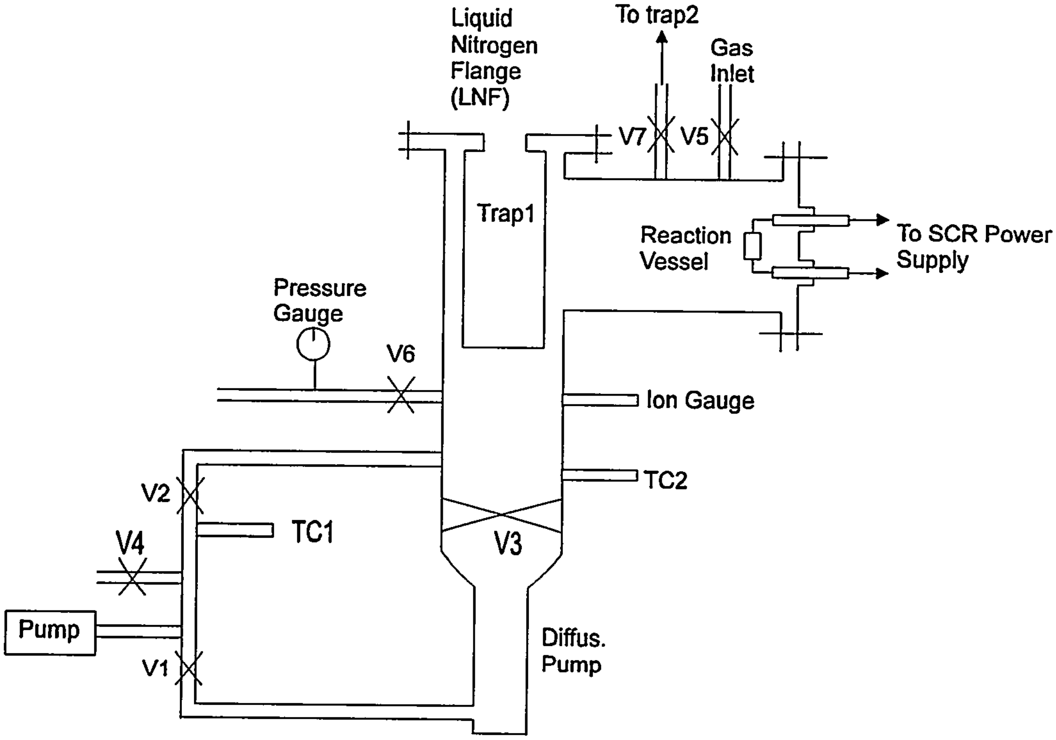


Figure 8 Vacuum reactor designed for SiO reaction

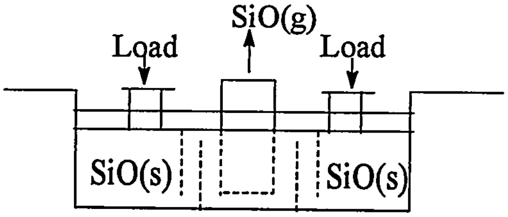


Figure 9 SiO evaporation vessel for vacuum reactor

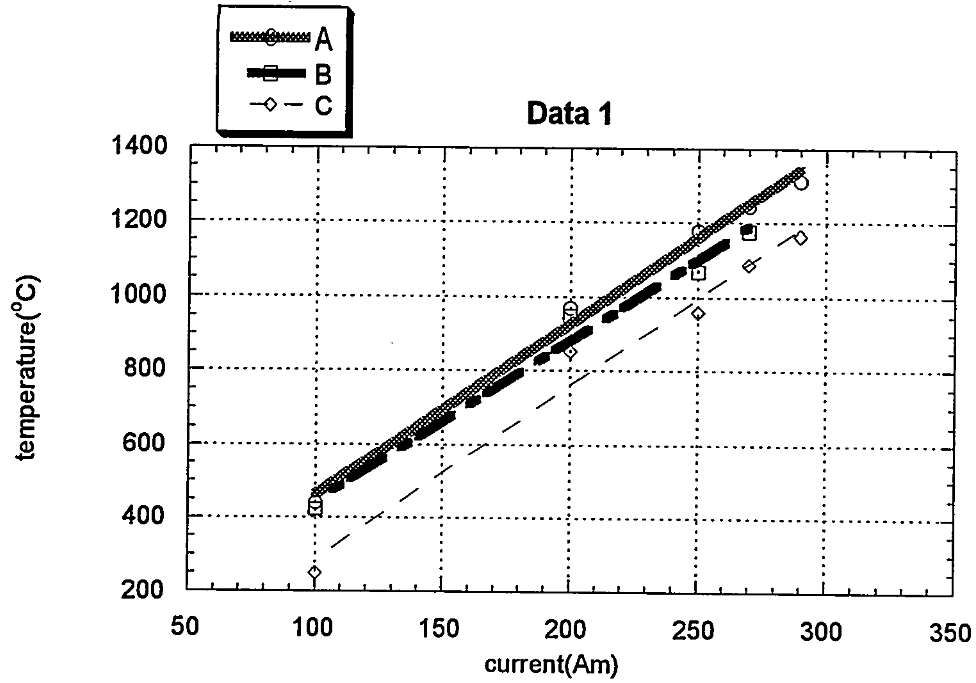


Figure 10 Temperature calibration lines for vacuum reactor. A) at 3×10^{-5}torr; B) in argon at 5×10^{-3}torr; C) in argon at atmosphere pressure.

experiments in this vacuum reactor were read from these calibration lines according to the current charged to the evaporation vessel.

The generation of SiO gas was proven by the weight loss of the evaporation vessel containing starting material. In high vacuum, 10^{-5} to 10^{-6}torr, 410 mg of weight loss was found when 1g of the commercial SiO powder was heated at 1170°C for one hour. Brown powder was deposit on the walls of the reactor. The MAS-NMR spectra of this brown powder exhibited a broad band, whose chemical shift peaked at – 200ppm. This result was consistent with the literature data for SiO. However, there was no weight loss under argon or helium atmosphere pressure in argon or helium when the evaporation vessel was heated at the same temperature, indicating no gaseous SiO formation under these conditions. When the vacuum was kept around 10^{-4}torr but a small amount of N_2 was introduced, the weight loss was found to be 0.42g for 1g starting material, similar to that obtained in aforementioned higher vacuum experiment. This result ensures the generation of SiO gas along with the introduction of other gases into the system. Therefore, several reactions have been studied under this condition.

Methane was first chosen to react with gaseous SiO because it is the simplest organic compound. As soon as the heating of SiO powder began, methane was introduced into the reactor at a flow rate that allowed the pressure to be kept at 10^{-4}torr. After 1 hour, a pump system connected to trap 2 was used to take out the volatile products, which could then be trapped in the liquid nitrogen trap 2. After the trap 2 was warmed to room temperature, 0.5mL deuterated chloroform was added to the trap. No product was detected by GC-MS. The ^{1}H-NMR revealed a sharp peak with a chemical shift at 0.08ppm, which could be signed to Si-CH_3, and a singlet with a chemical shift at 1.56ppm due to a proton in –OH or H_2O. No Si-H was detected. According to this result, silicon did insert into C-H bond. However, it was difficult to fully characterize the product due to the trace amount and poor repeatability. Therefore, the mechanism for the insertion of Si was not clear. The brown powder deposited on the walls of nitrogen trap 1 was extracted with deuterated chloroform. The ^{1}H-NMR study of the extract showed a bunch of peaks with chemical shifts in the range of 0-2ppm. The methane probably polymerized at such a high temperature.

Phenylacetylene was the second compound charged into the SiO vacuum reactor to react with SiO gas. After a one-hour reaction, only starting material was trapped in liquid nitrogen trap 2. On the walls of liquid nitrogen trap 1, a reddish polymer was collected. This polymer was insoluble in common organic solvents, so the full identification of its structure is impossible. The IR spectra had a small peak at 2163 cm^{-1}, which could be assigned either to an unreacted triple bond or a Si-H bond. A hump at 1072 cm^{-1} may due to Si-O stretches. The elemental analysis of the reddish polymer showed it contained 77.67% carbon and 5.23% hydrogen. Thus 17.1% content belongs to other elements. In this experiment condition, silicon and oxygen from SiO gas was the only source of this portion. However, based only on these results, we could not discern the nature of the incorporation of SiO in the red polymer.

When isobutene was used to react with the SiO gas generated in the vacuum reactor, nothing other than starting material was collected in liquid N_2 trap 2. An insoluble white polymer was deposited on the walls of liquid N_2 trap 1. The IR spectrum of this white polymer revealed broad peaks around 3500 cm^{-1} and 1100 cm^{-1}, indicating the presence of Si-O and O-H bond in this polymer. C-H bond showed up at 2800 cm^{-1}-2900 cm^{-1}. However, there was no Si-H bond involved, because no peak around 2100 cm^{-1} was observed. Again, gaseous SiO generated from the reaction vessel was the only source for the silicon and oxygen incorporated into the polymer. Due to its low solubility in organic solvent, the polymer should be a cross-linked network rather than linear poly(isobutene). But its poor solubility introduced much more difficulty in full characterization of this white polymeric material. Therefore, the role of SiO in this reaction also remains unknown.

We realized, at this point, although the generation of gaseous SiO was successful by using the high vacuum reactor, the polymerization of organic compounds, which resulted in insoluble network, was inevitable. We tried to modify the reactor by adding some shields around the evaporation vessel in order to block the radiated heat, but still only insoluble polymers were obtained. Another problem associated with the vacuum reactor was the low concentration of reactants. The molecules of the organic compounds had less of a chance to find molecular SiO in the gas phase.

<u>Generation and reactions of SiO in 'tube furnace' reactor</u> Because of the above concerns, we switched to a 'tube furnace' reactor. In this reactor, gaseous SiO generated in the hot zone can be carried out by an inert gas flow and should react with other organic compounds in a zone with a relatively lower temperature. (Figure 11)

Since it was difficult to get gaseous SiO at atmosphere pressure, according to our previous experiments, could SiO evaporate under the argon flow condition in the 'tube furnace'? The argon flow in high rate through the reactor may remove SiO gas from where it formed thus lower the partial pressure of SiO and let the reaction (Scheme 37) shift to the right side.

At the very beginning, when high purity argon was used as delivered without further purification, small beads of silicon metal were found in the boat containing unreacted starting material after a thermal treatment at 1200°C for 1 hour. Then we purified the argon by passing it through another tube furnace packed with metal chips before inlet to the reaction furnace. No silicon beads were found when the purified argon was used and the percent weight loss of SiO powder after heated at 1200°C for 1hour was 24%. This evaporation rate was good enough for the investigation of the

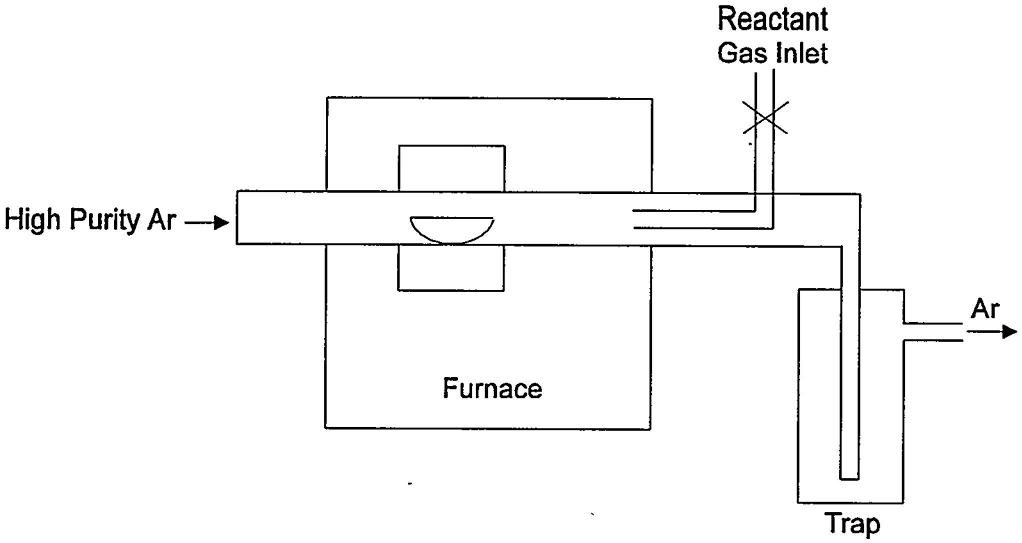


Figure 11 'Tube furnace' reactor designed for SiO reactions

$$\mathrm{SiO\,(s)} \rightleftharpoons \mathrm{SiO\,(g)}$$

Scheme 37 The equilibrium between solid and gaseous SiO reactivity of gaseous SiO towards other organic compounds.

Naturally, the next question was whether the gaseous SiO can stay in single molecular state for a time long enough to allow it to encounter with other organic compounds. To answer this question, both isobutene and acetone were utilized to react with SiO in the 'tube furnace' reactor. Isobutene was introduced to the reaction zone via the 'reactant gas inlet' tube and any products together with the unreacted starting material were carried out by argon flow and were trapped in the liquid nitrogen trap. After the evaporation of unreacted isobutene from the trap, some yellow solid was left. Unfortunately, GC-MS and ^{1}H-NMR only gave a whole bunch of unsolvable peaks.

In the case of acetone, the starting material was loaded in the trap and the high purity argon containing SiO was bubbled into it for about 1 hour. After the removal of the acetone, only very small amount of residue was obtained. It was a terrible mixture according to GC-MS. The attempts to separate this mixture on a preparation GC failed. The major disadvantage of this reactor is that only a very small amount of products can be trapped, which caused big challenge in separation and identification of these products.

Evaporation of SiO in 'metal Atom' Reactor. This reactor was donated by General Electric Company (Figure 12).

We tried several times to generate gaseous SiO in this reactor and found the efficiency of the evaporation was extremely low. It seemed impossible to get the alumina container heated to a temperature high enough to obtain efficient evaporation. So we had to give up without trying any reactions.

Initial research on microwave facility The utilization of microwave radiation to evaporate SiO is a completely new idea. It is very attractive because a high temperature can be achieved in a certain material without over-heating other species present, if they absorb at different frequencies. Therefore, it may give cleaner products when the gaseous SiO generated in this way reacts with other organic compounds, avoiding high temperature by-products. The basic configuration for our microwave reactor, a slotted wave-guide processing, is illustrated in Figure 13.

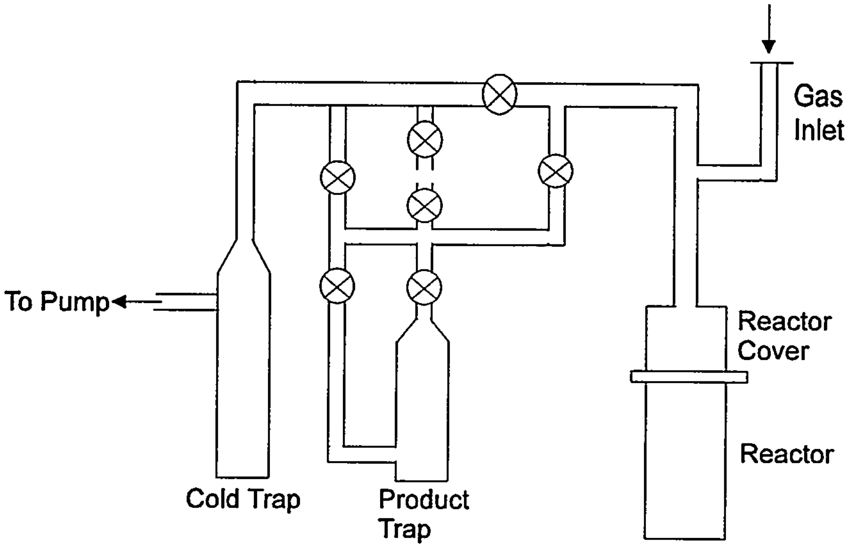


Figure 12 'Metal Atom' reactor modified for SiO reactions

Unfortunately, the SiO powder does not absorb at 915 or 2450 MHz, which were the only frequencies generated by our microwave facility. No weight loss was observed when the SiO powder was irradiated for 0.5 hour. The alumina boat containing the SiO powder was only slightly warmed. So our microwave facility was not able to evaporate SiO. Although the microwave idea is promising, much more effort is necessary in order to find the suitable frequencies at which the evaporation of SiO can be successfully carried out.

<u>Initial study of germanium monoxide</u> During the research on SiO, some of our efforts were turned towards its germanium analogue, germanium monoxide (GeO). The existence of this compound has not been well established and we need more information about it for purely scientific reasons.

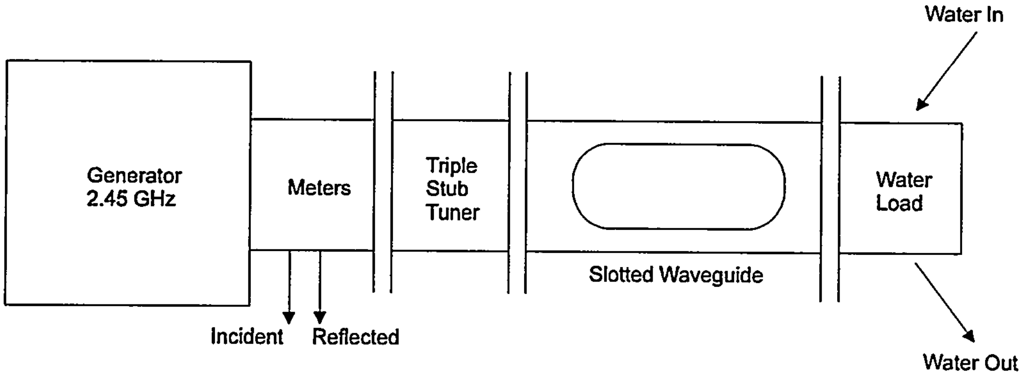


Figure 13 Illustration of microwave reactor

The formation of GeO, according to the reaction shown in Scheme 38, was

$$\mathrm{Ge} + \mathrm{GeO_2} \longrightarrow 2\,\mathrm{GeO}$$

Scheme 38 Formation of GeO by reaction of Ge and GeO_2

carried out in vacuum reactor at 800°C at a much faster rate compared to the formation of SiO. The covers of the evaporation vessel were pushed out if the temperature was not raised slowly enough. The same reaction was also achieved in the 'tube furnace' reactor and monitored on a TGA (Figure 14).

A yellow powder was collected from the walls of the reactors. However, the XRD pattern of the yellow powder indicated that it was a mixture of germanium and

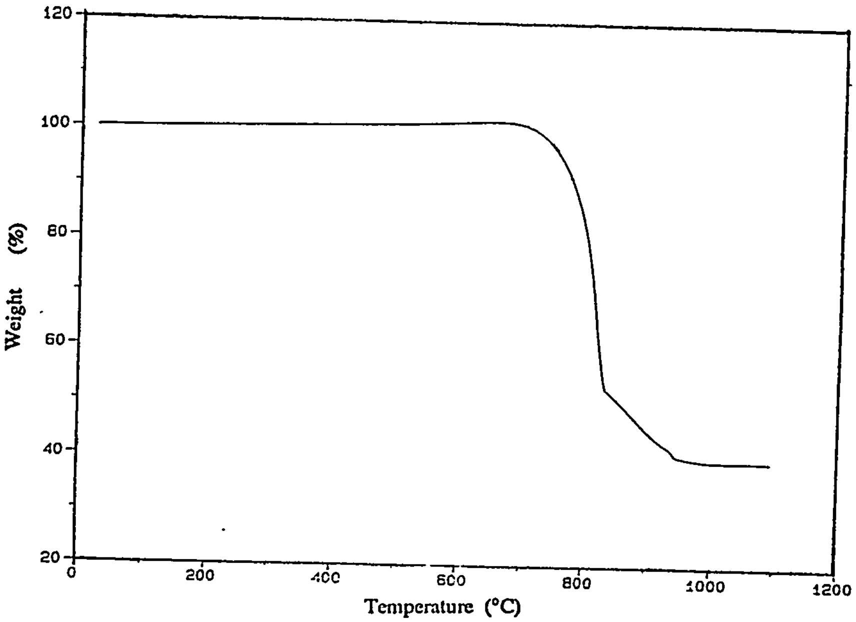


Figure 14 TGA of the mixture of Ge and GeO_2 (mole 1:1)

germanium dioxide. The disproportionation of GeO could occur when it deposited onto the surface of the reactor (Scheme 39).

$$2\,\mathrm{GeO} \longrightarrow \mathrm{Ge} + \mathrm{GeO_2}$$

Scheme 39 Disproportionation of GeO

Conclusions

Four kinds of reactors, including a high vacuum reactor, a 'tube furnace' reactor, a 'metal atom' reactor, and a microwave reactor, were built and modified to study the reactions of gaseous SiO with organic compounds.

The evaporation of SiO powder in a high vacuum reactor gave 40% yield of gaseous SiO. The reaction of gaseous SiO with isobutene resulted in an insoluble white polymer, whereas, an insoluble red polymer was obtained when SiO reacted with phenylacetylene. The incorporation of SiO into these polymers was indicated by spectroscopy data but the mechanism for the insertion of SiO was not clear.

A 20% yield was obtained when the evaporation of SiO was carried out in a 'tube furnace' reactor. The reaction of SiO(g) with isobutene and acetone in this reactor only gave trace amounts of mixtures that could not be separated and identified.

The 'Metal atom' and microwave reactors were not able to evaporate SiO powder.

Experimental

The Characterizations of synthesized compounds were based on IR, ^{1}H and ^{13}C-NMR spectra. ^{1}H and ^{13}C-NMR spectra were acquired on a Varian VXR 300 spectrometer in deuterated chloroform solution. The infrared spectra were recorded on an IBM IR-90 series FTIR spectrometer. TGA analyses were performed on a Du Pont modal 951 thermal analyzer in Argon atmosphere and 20°C/min. heating-rate unless otherwise specified. X-ray powder diffraction spectra were obtained on SCINTAG XDS-2000 generator.

Commercially available reagents were used as received from Aldrich or Fisher Chemical Co. without further purification unless specified otherwise.

Generation of gaseous SiO in vacuum reactor 1.0g commercial silicon monoxide powder was loaded equally to the two containers of the evaporation vessel (SO-22, R. D. Mathis Company). After the insertion of the vessel to the Electrical Feed-though Flange (EFF) and then the EFF to the vacuum reactor, mechanical pump 1 and oil diffusion pump 1 were used to achieve a vacuum of 10^{-5}-10^{-6}torr inside the reactor. Cooling water was applied to the outside walls of the oil diffusion pump and the reactor chamber. Liquid N_2 was added to trap 1 in order to create the cold surface, on which gaseous SiO can deposit. Then DC power was turned on and the current was slowly raised to 250Am. After remaining at 250Am for about 1 hour, the current was turned down gradually and the power supply was finally removed. Then the V3 and V_2 were closed and inert gas was introduced to the reactor through V5. After atmospheric pressure was reached, the EFF was opened and the reactor vessel was weighed to give 410mg weight loss (41%). Brown powder was collected from the walls of the reactor and trap 1. This brown powder is amorphous according to its XRD pattern.

Reaction of gaseous SiO with CH_4 in the vacuum reactor The gaseous SiO was generated following the procedure described above. After the current had been set at 250Am for 10 minutes, methane was introduced into the reactor via the gas inlet pipe at a rate that would not let the pressure exceed 10^{-4}torr. The reaction was carried out for 1 hour and liquid N_2 was added to trap 1 during this period of time. After the reaction was stopped by the removal of power, V3 and V5 were closed and V7 was opened. Any volatile products were led out and trapped into liquid N_2 trap 2, while liquid N_2 in trap 1 was blow away. (Figure 8) The trace amount of product collected in trap 2 was characterized by ^{1}H-NMR(δ, ppm): 1,56 (s), 0.08 (s). The soluble material extracted from the powder deposit on the walls of trap 1 was a mixture of alkanes. FTIR (cm^{-1}): 3076 (w), 3024 (w), 2924 (m), 2855 (w), 2163 (m), 1597 (m), 1492 (m) 1072 (s).

Reaction of gaseous SiO with isobutene A procedure similar to the reaction of SiO with methane was used in this reaction. A white insoluble polymeric material was obtained from the walls of liquid N_2 trap 1. Only FTIR data was taken for this polymer. FTIR (cm^{-1}): 3500 (broad, m), 2910 (m), 1100 (broad, s).

Reaction of gaseous SiO with phenylacetylene A similar procedure to the reaction of SiO with methane was used in this reaction, except that the phenylacetylene was pumped into the reactor through V7. An insoluble reddish polymer was deposited on the walls of liquid N_2 trap 1. FTIR (cm^{-1}): 3400 (broad, m), 1100 (broad, vs), 500 (s).

Generation of gaseous SiO in a 'tube furnace' reactor 1.2g commercial SiO powder was loaded into an alumina boat and was put in the middle of the hot zone of the 'tube furnace' reactor. High purity argon, which was purified by passing through a pre-furnace packed with metal chips, was continuously flow through the reactor. The temperature was raised to 1200°C at a rate of 20°C/min and had been holding at 1200°C for 1 hour, then cooled to room temperature at -10°C/min. The weight loss was found to be 2.85g. (24%) XRD (2θ, degree):28.5 (90%), 47.5(42%).

Reaction of SiO with isobutene in a 'tube furnace' When the furnace temperature was raised to 1200°C and the gaseous SiO was generated, isobutene was charged to the reactor via the gas inlet pipe. All the compounds, including SiO, unreacted isobutene and any possible products, were carried out by argon flow and were trapped by a liquid N_2 trap. After evaporation of the unreacted isobutene, the residue was checked by GC-MS, which revealed a set of unseparable peaks. No major product was identified.

Generation of GeO in the 'tube furnace' Germanium powder (0.73g, 10mmol) and germanium dioxide (1.06g, 10mmol) was mixed. The mixture was loaded to an alumina boat and was put in the middle of the hot zone of the 'tube furnace' reactor. High purity argon, which was purified by passing through a pre-furnace packed with metal chips, was continuously flow through the reactor. The furnace temperature was raised to 700°C at a rate of 10°C/min and then at 5°C/min to 800°C. After heating at 800°C for 1.5 h, the system was cooled to room temperature at -10°C/min. The weight loss was found to be 1.54g. (86%) Yellow powder was collected from the walls of the tube. XRD (2θ, degree):21.5 (20%), 26.0 (100%), 27.5 (85%), 36.0(10%), 38.0 (20%), 39.5 (11%), 41.7(15%), 45.5 (18%), 49 (10%), 53.9 (18%) 59 (9%).

GENERAL CONCLUSIONS

In the first section of this thesis, we successfully synthesized a series of polycarbosilanes, polysilanes and related copolymers as SiC ceramic precursors. The polymeric precursors were characterized by ^{1}H and ^{13}C NMR, FTIR, GPC and TGA. The resulting SiC ceramic materials were studied on XRD and elemental analysis. The SiC ceramic materials obtained from the stoichiometric precursor polymers contained less excess carbon compared to their analogues with phenyl pendent groups.

In the second part of this thesis, four different reactors were utilized in order to generate gaseous silicon monoxide. Among them, the high vacuum reactor and 'tube furnace' reactor were efficient for SiO evaporation. The reactions of gaseous SiO towards organic compounds were also studied. The roles of SiO in these reactions were not clear because of a lack of complete characterization of the products.

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