Chapter 1
Introduction
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The introductory chapter presents an overview of the developments in the area of preceramic polymers with a special reference to polysilahydrocarbons and polyborosiloxanes. A brief account of end-uses of preceramic polymers is given. The chapter concludes with the objective and scope of the present investigation.
The field of polymer science forms one of the major areas of molecular and materials science. This field impinges on nearly every aspect of modern life, from electronics technology, to medicine, to the wide range of fibers, films, elastomers and structural materials on which everyone depends. Most of these polymers are organic materials where the long-chain backbones consist mainly of carbon atoms linked together or separated by heteroatoms such as oxygen or nitrogen. Organic polymers are derived from petroleum and less frequently from plants, animals and microorganisms. Hence, they are generally accessible in large quantities and at moderate cost.

In spite of the widespread importance of organic polymers, attention is being focused increasingly towards polymers that contain inorganic elements as well as organic units in their backbone. Such polymers, referred to as inorganic or organometallic polymers, overcome many of the disadvantages of organic polymers. Most of the organic polymers react with oxygen or ozone over a long period of time and lose their advantageous properties. Organic polymers, in general, have poor thermooxidative stability and undergo degradation when exposed to ultraviolet or gamma radiation. On the other hand, inorganic and organometallic polymers possess excellent high temperature properties, thermooxidative stability and radiation resistance. Other advantages include fire resistance, chemical inertness and resistance to free radical cleavage.¹

The polymers which contain only inorganic elements in the polymer backbone are called “inorganic polymers”, whereas the ones which contain metallic elements along with organic units in their backbone are called “organometallic polymers”. Truly speaking, there appears to be no clear-cut demarcation between these two categories and quite often they are used interchangeably.

Inorganic and organometallic polymers find wide range of applications as high temperature coatings, thermal protective systems, matrix resins, high temperature elastomers and precursors for ceramics, due to their excellent high temperature properties and thermooxidative stability. In the last three decades considerable attention is paid towards using these polymers as precursors for
ceramics. Inorganic and organometallic polymers capable of giving high ceramic residue (50% or above) on heat treatment in inert atmosphere are called "preceramic polymers".

Following the first report by Yajima et al.\textsuperscript{2} that disclosed the use of polycarbosilane derived from polydimethylsilane as a precursor for SiC fiber, wide variety of inorganic and organometallic polymers have been reported as precursors for ceramics. Polysilanes, polycarbosilanes, polysilahydrocarbons, polycarbosilazanes, polysiloxanes, polyborazines, polycarborane-siloxanes, borosiloxanes etc. have all been explored as precursors for ceramics. The developments in the area of preceramic polymers have been discussed in various reviews.\textsuperscript{3-9}\textsuperscript{} In view of the voluminous literature available on this topic, it is rather difficult to discuss all the developments in detail. Hence, the introductory chapter of the present thesis provides only an overview of the important developments in the area of preceramic polymers. While presenting the literature, emphasis is laid on silicon, and silicon and boron containing polymers as the thesis deals with polysilahydrocarbons and borosiloxanes.

1.1 Silicon containing polymers

1.1.1 Polysilanes

Polydiorganosilylenes commonly referred to as polysilanes is relatively a new class of inorganic polymers having an all silicon backbone. The first polysilane was probably prepared by Kipping\textsuperscript{10,11} in the early 1920s by the dechlorination of diphenyldichlorosilane (DPDCS) using sodium. But it was infusible and insoluble. Bukhard\textsuperscript{12} synthesized polydimethylsilane (PDMS) from dimethyldichlorosilane (DMDCS), using a similar procedure, which also suffered from the same problem as in the case of polydiphenylsilane. This led to the neglect of this field until Yajima and coworkers\textsuperscript{2} in 1975 reported the conversion of intractable PDMS by heat treating it in an autoclave to a processable polycarbosilane.

West and coworkers\textsuperscript{3,13-17} prepared soluble copolymers from methylphenyldichlorosilane (MPDCS) and DMDCS by Wurtz reaction with sodium. A copolymer obtained with an equimolar ratio of MPDCS and DMDCS is called
“polysilastrene” (Structure 1) due to its structural resemblance with polystyrene and it exhibits a bimodal molecular weight distribution with a molecular weight ($\tilde{M}_w$) of ~ 50,000.

\[
\begin{array}{c}
\text{CH}_3 \\
\text{Si} \\
\text{CH}_3
\end{array} \quad \begin{array}{c}
\text{C}_6\text{H}_5 \\
\text{Si} \\
\text{CH}_3
\end{array}
\]

where $x/y = 1$

Structure 1

Alkali metals such as sodium and potassium are generally employed for the dechlorination$^5$ whereas lithium favors the formation of cyclic products. Use of catalytic amount of crown ethers (18-crown-6 or 15-crown-5) along with sodium is found to enhance the polymer yield and change the molecular weight distribution from bimodal to monomodal.$^{18-22}$

Polysilastrene after crosslinking by UV irradiation gave ~30% ceramic residue on pyrolysis and the poor ceramic residue was attributed to incomplete crosslinking.$^{15}$ Schilling et al.$^{23-25}$ described the synthesis of vinyl-functionalized polysilane by reacting methylvinylidichlorosilane (MVDSC), DMDCS and trimethylchlorosilane (TMCS) with sodium in an inert solvent and also the formation of polysilanes containing Si-H and Si-vinyl functional groups by dechlorinating methyldichlorosilane (MDCS) with MVDSC and TMCS in presence of sodium in toluene/THF mixture.

Functionalization of polysilanes drastically influences their solubility, $T_g$, cure kinetics and ceramic residue.$^{26-28}$ In recent years, polymethylsilane, synthesized by dechlorination of MDCS has been studied extensively as a promising precursor to SiC$^{8,29-52}$ because of its ideal stoichiometry. However, polymethylsilane gives lower ceramic yield on pyrolysis. Several authors focused on the role of Si-H bonds in polymethylsilane for improving the final ceramic yield by promoting crosslinking.$^{8,38-46}$ In order to improve the ceramic yield, polymethylsilane-based precursors were used in presence of crosslinking agents.
such as boron containing catalysts\textsuperscript{31,35,36,41,49} and metallocene\textsuperscript{26} which enhanced the precursor processability and ceramic yield. When metallocene was used as a catalyst, long reaction time and high pressure were required.  

Iseki et al.\textsuperscript{52} reported a reflux heat treatment as a simple and effective procedure to enhance the ceramic yield without using catalysts or high pressure. The reflux process is an effective way to convert linear Si-Si units into CSiSi\textsubscript{3} units prior to carrying out Kumada’s rearrangement.\textsuperscript{53} Gon et al.\textsuperscript{54} reported a method for enhancing the molecular weight of polymethylsilane at 70°C by carrying out the synthesis in the presence of polyborazine. 

Polymethylsilane is, however, not sufficiently oxygen stable and is often flammable in air at room temperature.\textsuperscript{47} In addition, polymethylsilane-derived ceramics contain considerable amount of silicon. Iseki et al.\textsuperscript{55,56} had overcome these problems by using poly(methylsilane-dimethylsilane) copolymers in place of polymethylsilane. These copolymers serve as matrix resins for ceramic matrix composites (CMCs). 

Radiation curing of polymethylsilane is now considered as an industrially viable method to produce high heat resistant SiC fibers with low oxygen content. \textsuperscript{56} Gamma-ray radiation curing studies of polymethylsilane and poly(methylsilane-dimethylsilane) precursor with improved ceramic yield were reported by Iseki et al.\textsuperscript{56} 

Apart from the classical Wurtz reaction, several novel electrochemical\textsuperscript{57-62} and ultrasonic methods\textsuperscript{21,63-65} have also been reported for the synthesis of polysilanes. Of late, synthesis of newer polysilanes and their characterization have been reported.\textsuperscript{66-76} Recently, a room temperature synthesis of polysilanes with high yield (50 to 83\%) was reported by Holder et al.\textsuperscript{77} 

\subsection{1.1.2 Polycarbosilanes} 

Polymers with backbone comprising of silicon and carbon are termed “polycarbosilanes”. Yajima et al.\textsuperscript{2,78-80} in their pioneering work, prepared polycarbosilane by heat treatment of dodecamethylcyclohexasilane (Me\textsubscript{2}Si\textsubscript{6}) or
polydimethylsilane in an autoclave in argon atmosphere at temperatures above 400°C under pressure (Scheme 1.1)

Scheme 1.1. Yajima's process

Yajima et al.\textsuperscript{81} studied the use of a catalyst, viz., borodiphenylsiloxane for the thermal conversion of PDMS to polycarbosilane at atmospheric pressure at 350°C. Habel et al.\textsuperscript{82} reported the use of poly(borodiphenylsiloxane) for converting polysilane containing methyl and phenyl groups to boron containing polycarbosilane. Polycarbosilanes were also prepared by ring opening polymerization of 1,3-disilacyclobutane\textsuperscript{83} and substituted 1,3-disilacyclobutanes\textsuperscript{83,84} using chloroplatinic acid as catalyst. Poly(diethylsilmethylene) having molecular weight (\(M_n\)) of 2,50,000 was prepared by the ring opening polymerization of 1,1,3,3-tetramethyl-1,3-disilacyclobutane with platinum catalyst.\textsuperscript{85} This polymer is thermally stable up to 600°C in inert atmosphere, but readily decomposes at 200°C in presence of air.
Seyferth and Lang\textsuperscript{86} synthesized polycarbosilanes with regularly substituted pendant Si-vinyl groups by the ring opening polymerization of 1-vinyl-1-silacyclobutane in tetrahydrofuran (THF) and hexamethyl phosphoramidite using butyllithium as a reducing agent. Polymers were obtained in 60-88\% yield and the molecular weight ranges from 6,000 to 11,000. They are stable up to 400°C and undergo decomposition above 450°C.

Pillot et al.\textsuperscript{87} explored the reductive coupling of dichlorodisilylmethane with alkali metal as a means of preparing polycarbosilane. Polycarbosilanes were also obtained by the dehalogenation of diorganodichlorosilanes with dihalomethanes using alkali metals.\textsuperscript{88}

Whitmarsh and Interrante\textsuperscript{89} studied the Grignard coupling of chloromethyltrichlorosilane (ClCH$_2$SiCl$_3$) by reacting with magnesium in diethylether. A branched polycarbosilane was formed when the chloroderivative was reduced with LiAlH$_4$. Habel et al.\textsuperscript{90,91} reported the reduction of halogenated poly(methylphenylsilmethylene) and poly(diphenylsilmethylene) with LiAlH$_4$ to obtain poly(hydridopolycarbosilane)s.

Schilling and co-workers\textsuperscript{29,92,93} synthesized branched polycarbosilanes from a vinyl-containing chlorosilane monomer. When dechlorination of MVDCS was carried out in presence of TMCS using potassium in THF, tetra(trimethylsilylated) compound was obtained as the major product.\textsuperscript{92} This suggests that vinyl group takes part in the polymerization. Schilling et al.\textsuperscript{29,93} synthesized branched polycarbosilanes by dechlorinating MVDCS with potassium in THF in presence of DMDCS or MDCS and TMCS.

Polycarbosilanes with ethylenic and acetylinic functionality were prepared from poly(dichlorosilmethylene).\textsuperscript{94,95} Poly(silaacetylene)s were prepared by reacting dilithioacetylene with diorganodichlorosilanes (RR'SiCl$_2$) [where R = Me or Ph] or with 1,2-dichlorodisilane (ClMe$_2$-Si-SiMe$_2$Cl).\textsuperscript{95} A silylenediacetylene polymer of high molecular weight was prepared by Maghsoodi and Barton\textsuperscript{96} starting from hexachlorobutadiene. Habel et al.\textsuperscript{97} reported the synthesis of poly(alkynylsilmethylene) containing the repeating unit, -SiR$_2$CH$_2$-, where
R= -C≡CH, -C≡C(CH₂)ₙCH₃ or -C≡C-C₆H₅. Uhlig reviewed the synthesis of new organosilicon polymers using silyl triflate intermediates. Proto-dephenylation of phenylated polysilanes as well as poly(silylenemethylene)s by triflic acid gave new functionalized compounds. Thermally stable polysilylenemethylenes with siloxane crosslinking moieties were successfully synthesized by Ogawa et al. with T₉ ranging from 15 to 20°C.

A wide range of new poly(silylenemethylene)s of the type [SiRR'CH₂]ₘ were prepared and their conversion to ceramic material was studied in detail. Kwak and Masuda found that the polymerization of p-(dimethylsilyl)-phenylacetylene in toluene at 25°C and 80°C using Rh₁(PPh₃) catalyst afforded highly regio- and stereoregular poly(dimethylsilylene)phenylene-vinylene)s.

Amoros et al. studied the reaction of poly(dimethylsilane) and poly(dimethylcarbosilane) with bis(cyclopentadienyl)M dichloride Cp₂MCl₂ (M= Ti, Zr, Hf) complexes to obtain precursors for SiC ceramics. Tsumura and Iwahara developed crosslinked polycarbosilanes with excellent mechanical properties by hydrosilylation curing of multi-functional vinylsilanes with hydrosilanes. Chemically modified polycarbosilanes containing organofluoric groups and Si-Al-C-O linkages with improved ceramic yield, were synthesized by Okuzaki et al. by reacting polycarbosilane with fluoric acid and aluminium triisopropoxide respectively. Cao et al. obtained dry-spinnable polycarbosilane by reacting the polycarbosilane, prepared by Yajima’s process, with 1 wt% of polyborazine at 300°C for 1 h. A hyperbranched polycarbosilane of the type [R₃SiCH₂]- [-SiR₂CH₂]- [-SiR(CH₂)₅]- [-Si(CH₂)₂] was prepared by Interrante et al. for end-use as an inorganic/organic hybrid material.

1.1.3 Polysilahydrocarbons

Polymers containing two or more carbon atoms between silicon atoms are referred to as “polysilahydrocarbons”. They were synthesized through the dechlorination of diorganodichlorosilanes in presence of vinyl or diene monomers (Scheme 1.2). Schilling et al. synthesized polysilahydrocarbons by dechlorinating diorganodichlorosilane in presence of styrene or isoprene.
Van Aefferden et al.\textsuperscript{112} and Packirisamy et al.\textsuperscript{113-115} synthesized polysilahydrocarbons by reacting DMDCS and styrene under dechlorination conditions. They observed that the copolymers contain alternating units of disilyl and styryl in the polymer backbone. Packirisamy et al.\textsuperscript{113-121} studied in detail the effect of monomer feed ratio and reactivity of diorganodichlorosilanes on the microstructure and mechanism of formation of polysilahydrocarbons through the dechlorination of diorganodichlorosilanes in presence of styrene. In the copolymers synthesized from styrene and DMDCS, disilyl and styryl/oligostyryl units alternate with each other for the monomer feed ratios (styrene:DMDCS) 0.5:1, 1:1 and 1.5:1. With further increase in concentration of styrene, i.e., for the monomer feed ratio of 3:1, no disilyl linkage was observed and the repeating units mainly consisted of monosilyl linkages separated by oligostyryl units. However, for styrene-MPDCS system, disilyl linkages separated by oligostyryl units were observed even when the monomer feed ratio (styrene:MPDCS) was 5:1. This is attributed to the higher reactivity of MPDCS compared to that of DMDCS. Microstructural analysis of polysilahydrocarbons supported the conclusion that disilyl reaction intermediates mediate the polymerization. When styrene is present in large excess, styryl reaction intermediates mediate the polymerization resulting in the formation of monosilyl linkages separated by oligostyryl units. A generalized structure of the polysilahydrocarbon synthesized from MPDCS and styrene is given in structure 2.

\begin{center}
\textbf{Scheme 1.2. Synthesis of polysilahydrocarbons}
\end{center}
Ambadas et al.\textsuperscript{122,123} synthesized a novel polysilahydrocarbon from a single source precursor. Dechlorination of 1,2-bis(chlorodimethylsilyl)ethane [BCDMS] in presence of potassium resulted in the formation of a polymer, poly(tetramethyldisilyleneethylene) (Structure 3) whereas no polymer was obtained when sodium was used for the dechlorination. This was attributed to the low reactivity of this monomer under dechlorination conditions. Interestingly, this monomer underwent dechlorination in presence of styrene.

Thus, it is obvious that depending on the reactivity of diorganodichlorosilane, either disilyl or styryl reaction intermediates mediate the polymerization. A typical structure of the polysilahydrocarbon synthesized from BCDMSE and styrene in presence of Na/18-crown-6 is given below (Structure 4).

Packirisamy et al.\textsuperscript{117} synthesized crosslinked polysilahydrocarbons by reacting MVDCS with styrene under dechlorination conditions. During dechlorination, vinyl group of MVDCS participates in the polymerization resulting
in the formation of crosslinks. A typical structure of poly(methylvinylsilylene-co-styrene) is given below (Structure 5).

![Structure 5](image)

Polysilahydrocarbons have poor thermal stability and give very poor ceramic residue (<20%). Sartori et al.\textsuperscript{124,125} explored the possibility of converting polysilahydrocarbon synthesized from DMDCS and styrene to thermally stable polycarbosilane by heat treating the polysilahydrocarbons at 385°C in an unconfined atmosphere under the flow of argon.

Packirisamy et al.\textsuperscript{115,126} studied the microstructure, thermal stability and ceramic conversion of polycarbosilanes obtained by heat treatment of polysilahydrocarbons in a partially confined environment. It was observed that the incorporation of small amount (<10 mole%) of methylphenylsilyl units in the copolymer containing dimethylsilyl and styryl units drastically improved the thermal stability and ceramic residue of polycarbosilane. This has been attributed to the phenylene insertion reaction taking place during heat treatment. A typical structure of the heat-treated polysilahydrocarbon is given below (Structure 6).

![Structure 6](image)
In the present investigation, thermal degradation kinetics of polysilahydrocarbons, synthesized by Ambadas\textsuperscript{122} and the polycarbosilanes derived from them,\textsuperscript{126} and the end-use of polysilahydrocarbons as atomic oxygen resistant coatings for low earth orbit space structures have been studied and they form the basis for the chapters 3.6 and 3.7.

Polysilahydrocarbons serve as potential candidates for liquid lubricants.\textsuperscript{127} This advanced space lubrication systems replace the currently employed perfluoropolyalkylethers, which promote metal corrosion and undergo degradation under boundary lubrication conditions. The properties of these polysilahydrocarbons can be tailored by varying the alkyl substituent.

Corriu et al.\textsuperscript{128-130} described the preparation of linear poly(silylethylene) from vinyl hydrogenosilane using platinum in charcoal as a catalyst. Catalytic hydrosilylation of ethynylsilanes \[(R_{2}HSiC≡CH), \text{ where } R=\text{Me, Et or Ph}\] with chloroplatinic acid was studied as a means of preparing polymers with ethylenic functional moieties in the backbone.

Wu and Interrante\textsuperscript{131} prepared poly(silethylene)s by the ring opening polymerization of 1,1,3,3-tetrachloro-1,3-dimethyl-1,3-disilacyclobutane using chloroplatinic acid or platinumdivinyltetramethyldisiloxane complex as a catalyst.

A new polysilahydrocarbon, viz., chemically crosslinked polysilastyrene was prepared by Krishnan et al.\textsuperscript{132} through the dechlorination of a monomer mixture containing DMDCS and MPDCS in presence of divinylbenzene. The crosslinked polymer on pyrolysis at 1500°C gave β-SiC.

In recent years, polysilarylenes and polycarbosilarylenes with excellent thermal stability have been reported.\textsuperscript{133-135}

1.1.4 Polysilazanes and polycarbosilazanes

Polymers with silicon-nitrogen linkages in their backbone are termed "polysilazanes".\textsuperscript{8,136,137} They are generally prepared either by ammonolysis or aminolysis of organochlorosilanes.
Introduction

Verbeek\textsuperscript{138,139} in his pioneering work, synthesized polysilazanes by aminolysis of chlorosilane monomers. Polysilazanes were prepared in a two step process involving amination of trichloromethylsilane followed by the thermal condensation of the product tris(N-methylamino)methylsilane.\textsuperscript{138-140} Aminolysis of DMDCS and methylamine following a similar procedure as above was carried out by Winter et al.\textsuperscript{141} Seyferth and Wisemann\textsuperscript{142} reported the synthesis of N-methylpolysilazane from methylamine and dichlorosilanes.

A perhydropolysilazane was synthesized by passing ammonia gas through a pyridine-dichlorosilane adduct.\textsuperscript{143} Polysilazanes were also prepared by reacting trichlorosilane with hexamethyldisilazane \[ (\text{Me}_3\text{Si})_2\text{NH} \].\textsuperscript{4} Seyferth et al.\textsuperscript{144,145} described in detail the ammonolysis of organodichlorosilanes. Ammonolysis of MeHSiCl\textsubscript{2} resulted in a cyclic silazane \((\text{MeSiNH})_3\text{NH}\) and a linear polymer (Scheme 1.3).

\[ \text{MeSiHCl}_2 + \text{NH}_2 \rightarrow \text{MeSiHCl}_2 \quad \quad \text{Et}_2\text{O}/0^\circ\text{C} \quad \quad \text{MeSiNH}_3 \quad \quad \text{KH}((\text{ii})\text{CH}_3\text{I} \rightarrow \text{Polymer} \quad \text{THF}/\text{RT} \]

Scheme 1.3. Synthesis of polysilazane

Seyferth et al.\textsuperscript{144} also reported the preparation of polysilazane free from carbon by reacting dichlorosilane \((\text{SiH}_2\text{Cl}_2)\) with gaseous ammonia in polar solvents like dichloromethane or diethyl ether.

Burns et al.\textsuperscript{146} prepared polysilazanes by the ring opening polymerization of cyclic silazanes prepared by ammonolysis and co-ammonolysis method. In the first route silacyclobutasilazane was equilibrated with chlorosilane to give a mixture of chloro end-blocked silazanes, which was ammonolyzed to obtain the desired substituted silacyclobutasilazane. In the second route, a mixture of 1,1-dichloro-1-silacyclobutane and a chlorosilane was co-ammonolyzed directly. Ammonolysis of a mixture of MeHSiCl\textsubscript{2} and MVDCS or allyldichlorosilane afforded vinyl- or allyl-functionalized polysilazane.\textsuperscript{145} The advantage of having a vinyl or allyl group is that it provides -C=C- functionality which can be crosslinked via hydrosilylation reaction.
Xu et al. synthesized a new kind of polysilazane precursor containing linear-cyclic structure from the dilitium chloride condensation reaction of hexamethylcyclotrisilazane lithium salts and 1,3-dichlorotetraorganodisilazanes \([\text{ClR}_1\text{R}_2\text{Si}]_2\text{NH}\). Bao et al. prepared a copolysilane-cyclodisilazane precursor which was then heated to 1650°C to obtain SiC and Si₃N₄. Kleebe et al. prepared different liquid polysilazanes with tailored molecular structures by ammonolysis of functionalized chlorosilanes. Pyrolysis of the polysilazanes resulted in the formation of amorphous SiCN ceramics.

Hydrosilylation between 1,1,3,3-tetramethyldisilazane and 1,3-divinyl-1,1,3,3-tetramethyldisilazane occurs rapidly at 90°C in the presence of Karstedt's catalyst (Pt-divinyltetramethyldisiloxane) to give large macrocyclic products. Similar observation was made by Son and Rasul when trimethylsilylated or methylated derivative of 1,3-divinyl-1,1,3,3-tetramethyldisilazane was reacted with 1,1,3,3-tetramethyldisilazane.

Trassl et al. prepared polyvinylsilazane, a precursor for SiCN ceramics, by ammonolysis of functionalized chlorosilanes. Pyrolysis under inert atmosphere at 1000°C led to the formation of an amorphous SiCN ceramic. A polymeric precursor for the Si₃N₄-SiC-Y₂O₃ ceramic system was synthesized by Sawai et al. by block copolymerization of perhydropolysilazane with hydroxy-polycarbosilane, followed by chemical modification with yttrium methoxide.

Polycarbosilazanes have alternating silicon, carbon and nitrogen units in their backbone. A polycarbosilazane was synthesized by heating a polysilazane obtained from the sodium reduction of a mixture of DMDCS and 1,3-dichloro-1,3-dimethyldisilazane. This polymer on pyrolysis gave SiC-Si₃N₄ mixed non-oxide ceramics.

1.1.5 Polysilylcarbodiimides

Kienzle et al. developed a new class of silicon and nitrogen containing polymers called "polysilylcarbodiimides". These polymers were prepared by reacting organochlorosilane with cyanamide. Polysilylcarbodiimides were also
prepared by reacting chlorosilanes with bis(trimethylsilyl)carbodiimide. These polysilylcarbodiimides can be transformed into amorphous silicon carbonitride ceramics with about 65% ceramic yield, by pyrolyzing them in an inert atmosphere at 1100°C. The advantage with these polymers is that no prior crosslinking is required before pyrolysis.

1.1.6 Polysiloxanes and polysilsesquioxanes

Polysiloxanes are unique among inorganic polymers. They are the most studied and the most important ones due to their commercial significance. The Si-O backbone of this class of polymers endows it with a variety of fascinating properties. The high strength of Si-O bonds is responsible for high thermal stability of polysiloxanes.

Diorganodichlorosilanes obtained by Rochow’s process, that starts from elemental silicon, are used for the synthesis of polysiloxanes. This compound with the general formula $R_2SiCl_2$, can be used for the preparation of a wide variety of polymers having both organic and inorganic character. On hydrolysis, $R_2SiCl_2$ gives dihydroxy structures, which readily condense to give basic repeating units (Scheme 1.4). The nature of the product mostly depends on reaction conditions.

\[
\text{Si} + 2RCl \xrightarrow{\text{H}_2\text{O}} R_2\text{SiCl}_2 \rightarrow \left(\begin{array}{c}
\text{R} \\
\text{Si} \\
\text{O} \\
\text{R}
\end{array}\right)_n
\]

where $R = \text{alkyl or aryl}$

Scheme 1.4. Synthesis of polysiloxane

Polysilsesquioxane is an example for highly crosslinked organic-inorganic hybrid material. Its inorganic cage frame work is made up of silicon and has the formula of $(\text{SiO}_{1.5})_n$ where $n = 8, 10$ or $12$. This inorganic cage is externally covered by organic substituents, which enhance their solubility in organic solvents. They are prepared by hydrolytic condensation (sol-gel process) of trifunctional organosilicon monomers.
Among various silsesquioxanes, the octaphenylsilsesquioxane (PhSiO$_{1.5}$)$_8$ (Structure 7), decaphenylsilsesquioxane (PhSiO$_{1.5}$)$_{10}$ and dodecaphenylsilsesquioxane (PhSiO$_{1.5}$)$_{12}$ systems are the most interesting ones because of their high temperature stability.

![Structure 7](image)

Polysiloxanes and silsesquioxane sol-gels were reported as precursors to ceramics such as siliconoxynitride$^{159}$, siliconoxycarbide$^{160-162}$ and SiC$^{163,164}$ and black glass matrices for composite materials.$^{164-166}$ Since 1987 attempts have been made to use siloxane polymers as precursors for ceramics and as binders for sintering of SiC monoliths.$^{167}$ The properties of these resins which make them attractive as binders are the following: i) facile synthesis, ii) thermal and aerobic stability for subsequent processing, iii) compatibility with the ceramic powder, iv) decomposition into stable ceramics comprising of SiC and C at temperatures below those required for sintering of SiC ($\sim 2000^\circ$C) and v) sufficient char yield thereby minimizing the amount of volatiles evolved in the pyrolysis.$^{163,168}$

White et al.$^{160}$ reported that heating (PhSiO$_{1.5}$)$_x$ gels to 1500$^\circ$C produced a partially crystalline mixture of $\beta$-SiC, SiO$_2$ and C as detected by XRD and IR. Babonneau et al.$^{169}$ reported NMR evidence for the formation of $\beta$-SiC from (Me$_2$SiO)$_x$ (SiO$_2$)$_{1-x}$.

Porous ceramics with open or closed porosity combine various interesting properties, like low density, low thermal conductivity and high specific strength.$^{170}$ Therefore, they are of interest for an increasing number of applications.
(e.g., thermal insulation, catalyst support, lightweight structures). Siliconoxy-carbide ceramics are favorable candidates to meet these requirements. They are commonly prepared by two techniques. One technique is based on the sol-gel process\textsuperscript{171} and the other method uses preceramic polymers such as polysiloxanes as starting materials. When polysiloxane is used the shrinkage in the ‘green body’, the undesired feature of the polymers from the sol-gel process, is avoided. Yet another advantage is that polysiloxanes are easily mouldable.\textsuperscript{172}

A series of trimethylsilyl end-functionalized aliphatic hyperbranched polymers were studied to template porosity in polymethylsilsesquioxane films prepared by heat treatment of a spin cast methylsilsesquioxane precursor.\textsuperscript{173} By varying the extent of the functionalization, ceramic foams with controlled pore sizes were obtained.

A number of polysiloxane resins filled with different oxide, carbide or metallic powders were investigated as precursors for ceramics.\textsuperscript{174-180} Thin-walled (wall thickness: 100–2000 µm) Si-O-C-N mono- and bilayered ceramic tubes were obtained by centrifugal casting of a suspension of Si and SiC powders in polyorganosiloxane/triethoxysilane solution.\textsuperscript{181} After centrifugal casting in a Teflon tube with a rotational speed of 2000 rpm and subsequent crosslinking at 130°C and 60 rpm, the tubes were pyrolyzed in argon or in nitrogen at 1400–1600°C. Bilayered tubes with controlled variation of porosity were obtained by overcasting the monolayer green tubes with a modified slurry composition.

Philipp\textsuperscript{182} evaluated polysiloxane formed by the controlled hydrolysis of tetraethoxysilane (TEOS) as a binder for the formation of an oxide ceramic compact. At high temperature, the oxide particles are held together via reaction bonded silicates formed from SiO\textsubscript{2} obtained from the pyrolysis of the precursor.

1.2 Boron containing polymers

The key developments in organosilicon chemistry led researchers to work on novel synthetic approaches leading to the development of innumerable boron containing polymers and to explore their end-uses in terms of technological advantages offered by them. Boron forms a number of polymeric materials with
many other elements involving particularly bonds of B with H, C, O, N and P. The high bond energy of some of these bonds is responsible for their high temperature stability. Majority of boron containing polymers are derived from borazine, carborane and decaborane.\textsuperscript{9,183,184} A few polymers have also been synthesized from vinylpentaborane and boric acid.

### 1.2.1 Polymers derived from borazines

A tractable polyborazine which can be used as a precursor for boron nitride ceramic was first reported by Taniguchi et al.\textsuperscript{185} Later, Sneddon et al.\textsuperscript{186,187} synthesized a processable polyborazine (also known as polyborazylene) by the thermolysis of liquid borazine in vacuum at 70°C (Scheme 1.5).

\begin{center}
\textbf{Scheme 1.5. Synthesis of Polyborazylene}
\end{center}

This polymer was obtained as a white powder in high yield (~90%). It has molecular weight ($\bar{M}_w$) of 7,600 and has a branched structure. Polyborazylenes serve as excellent precursors for boron nitride ceramics.\textsuperscript{188} Boron nitride was obtained by heating this polymer in either argon or ammonia. Narula et al.\textsuperscript{189} synthesized poly(borazinylamine), by adding excess ammonia to cold toluene solution of B-tris(dimethylamino)borazine ([Me$_2$N]BNH)$_3$.

Kimura et al.\textsuperscript{190} studied the ammonolysis of B-tris(diethylamino)borazine in liquid ammonia at room temperature and obtained a crystalline solid B,B',B''-triaminoborazine [(H$_3$N.BNH)$_3$]. This solid undergoes rapid deamination at 120°C forming a slightly soluble polymer.

Synthesis of substituted borazines such as B-triamino-N-triphenylborazine, B-triamino-N-trimethylborazine and B-trianiloborazine has also been reported.\textsuperscript{191,192}
Paine et al.\textsuperscript{193,194} and Paciorek et al.\textsuperscript{195,196} prepared poly(borazinylamine) by reacting B,B',B''-trichloroborazine with hexamethyldisilazane in ether medium or in a hydrocarbon solvent. Pyrolysis of this polymer in vacuum at 1200°C resulted in the formation of turbostatic hexagonal boron nitride [(h)-BN].

Maya\textsuperscript{197,198} synthesized polyaminoborazines through the condensation of triethylborane or tris(dimethylamino)borane with polyfunctional amines such as 4,4'-methylenedipyrazole, 1,2-phenylenediamine, 3,3-diaminobenzidine and diethylenetriamine. These polymers were used as precursor for boroncarbonitride (BCN) ceramics.

Sneddon et al.\textsuperscript{199-201} prepared poly(β-vinylborazine) by solution polymerization of β-vinylborazine with a free radical initiator azobisisobutyronitrile (AIBN). β-Vinylborazine was obtained through the reaction of borazine with acetylene in presence of Wilkinson’s catalyst [RhH(CO)PPh\textsubscript{3}]. Pyrolytic decomposition of poly(vinylborazine) in ammonia at 1200-1400°C produced white crystalline h-BN. Preparation of poly(styrene-co-β-vinylborazine) by reacting β-vinylborazine with styrene in presence of AIBN has also been reported.\textsuperscript{201}

Perdigonmelon et al.\textsuperscript{202} prepared BN catalyst supports from molecular precursors and demonstrated the influence of the precursor on the properties of BN ceramic. Fine powders and foams of boron nitride have been prepared from various molecular precursors for use as noble metal supports in the catalytic conversion of methane. A molecular precursor derived from trichloroborazine (TCB), after reaction with ammonia at room temperature and then thermolysis up to 1800°C, gave BN. The aminoborazine-derived precursors when thermolyzed gave BN, expanded like foam.

Toury et al.\textsuperscript{203} prepared boron nitride fibers from symmetric and asymmetric alkylaminoborazines. The thermolysis of 2,4,6-[[CH\textsubscript{3}]\textsubscript{2}N]\textsubscript{2}B\textsubscript{3}N\textsubscript{3}H\textsubscript{5}, 2,4-[[CH\textsubscript{3}]\textsubscript{2}N]-6-(CH\textsubscript{3}HN)B\textsubscript{3}N\textsubscript{3}H\textsubscript{3} and 2-[[CH\textsubscript{3}]\textsubscript{2}N]-4,6-(CH\textsubscript{3}HN)\textsubscript{2}B\textsubscript{3}N\textsubscript{3}H\textsubscript{3} led to different types of polyborazines. Polyborazine filaments were prepared and subjected to thermal treatment up to 1800°C to obtain h-BN fibers.
1.2.2 Decaborane(14)-based polymers

The reaction of decaborane(14), $\text{B}_{10}\text{H}_{14}$, with Lewis bases (ligands, L) was reported for the first time by Schaeffer in 1957. Following this discovery, a number of such derivatives were prepared using various nitriles, amines, phosphines, sulfides and other ligands. In the formation of $\text{B}_{10}\text{H}_{12}\text{L}_{2}$ (Scheme 1.6), hydrogen atoms at 6 and 9 position of the $\text{B}_{10}\text{H}_{14}$ framework are displaced by electron pair donor atoms.

Incidentally, the ligand, L, in $\text{B}_{10}\text{H}_{12}\text{L}_{2}$ can be displaced by another ligand having a higher bonding strength, thus offering an alternative synthetic route for the synthesis of bis(ligand adduct)s of decaborane. It is obvious that if a bidendate ligand is used in place of L for the synthesis of $\text{B}_{10}\text{H}_{12}\text{L}_{2}$, a linear polymer can be obtained. (Scheme 1.7)

Following the report by Parshall on the synthesis of a decaborane-based linear polymer from P,P,P',P'-tetraethylenediphosphine, various polymers were synthesized from Lewis bases such as phosphines, nitriles and amines.

Polymeric Lewis base adducts of decaborane can be prepared in organic solvents such as benzene, hexane, toluene, xylene, diethylether and THF.
Most of these polymers are soluble in polar solvents such as dimethylacetamide (DMAc), dimethylformamide (DMF), N-methylpyrrolidone (NMP), hexamethylphosphoramide (HMPA) and dimethylsulfoxide (DMSO). The solubility of these polymers appears to depend on the nature of the bridging ligand.

In general, \([B_{10}H_{12}.L_{n}]\) polymers give high char residue (70-90%) in inert atmosphere. The fact that these polymers lose very little weight on pyrolysis suggests the presence of "thermolabile functionality".\(^{207}\) In the case of \([B_{10}H_{12}.L_{n}]\) polymers, the acidic bridging B-H-B bonds of the B\(_{10}\)H\(_{12}\).L\(_2\) cage unit may serve as "thermolabile functionality". On thermal treatment, B\(_{10}\)H\(_{12}\).L\(_2\) cage may be converted into (LH\(^+\))\(_2\) B\(_{10}\)H\(_{10}\).\(^2-\).

Seyferth and Rees\(^{207}\) reported that decaborane-based polymers undergo degradation in DMAc. Packirisamy et al.\(^{208,209}\) studied the effect of various polar solvents on the stability of these polymers using \(^{11}\)B-NMR spectroscopy. \(^{11}\)B-NMR spectra of the decaborane-based polymers were recorded in DMF and DMSO. It was found that the polymer has undergone degradation in these solvents resulting in the formation of more than one degradation products. One of the main degradation products is B\(_{10}\)H\(_{10}\).\(^2-\). Studies revealed that there is no salt formation during the synthesis, but on standing the complex incorporates oxygen resulting in the formation of small amount of the salt. Polar solvents favor proton transfer from B\(_{10}\)H\(_{12}\) cage of a B\(_{10}\)H\(_{12}\).L\(_2\) complex to the ligand and in a less polar solvent such a proton transfer is less favored. The proton transfer mechanism which is operative in polar solvents is shown below:

\[
B_{10}H_{12}.L_2 \leftrightarrow B_{10}H_{12}.L + L
\]
\[
B_{10}H_{12}.L + \text{Base} \to B_{10}H_{11}^- + [\text{Base.H}^+] + L
\]
\[
B_{10}H_{11}^- + \text{Base} \to B_{10}H_{10}^{2-} + [\text{Base.H}^+]
\]

Packirisamy et al.\(^{9,208,209}\) synthesized B and Si containing polymer which is the first decaborane polymer reported soluble in THF (less polar solvent compared to DMAc, DMF and DMSO) through the reaction of decaborane with 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane and evaluated it as an atomic oxygen (AO) resistant coating for low earth orbit space structures.
Decaborane-based polymers serve as precursors for boron nitride and boron carbide ceramic materials\textsuperscript{9,210-213} and as atomic oxygen resistant coatings.\textsuperscript{9,208,209} Ambadas\textsuperscript{122} synthesized B and Si containing polymers through the reaction of decaborane with different types of aminosiloxanes, namely, 3-aminopropyl-triethoxysilane (APTEOS), 3-aminopropylmethylidethoxysilane (AMDEOS) and aminopropyl terminated polydimethylsiloxane (APPDMSiO).

New decaborane-based, single-source molecular and polymeric precursors to $\text{B}_4\text{C}$ were developed by Sneddon et al.\textsuperscript{214} that enable the formation of boron carbide in processed forms, including nanofibers, nanocylinders and nanoporous materials. Sneddon et al.\textsuperscript{215,216} reported the synthesis, characterization and ceramic conversion of a polyborosilazane that can be prepared via the reaction of commercially available polysilazane, namely CERASET\textsuperscript{®}, with decaborane. Depending on the pyrolysis conditions, these new polymers can serve as excellent precursors to SiC/BN ceramic compositions.

Forsthoefel and Sneddon\textsuperscript{217} obtained metal boride precursors by dispersing metal oxides in decaborane-dicyanopentane polymer. Pyrolysis of the metaloxide/polymer dispersions gave metal borides, including $\text{TiB}_2$, $\text{ZrB}_2$ and $\text{HfB}_2$ in high yield. Metal-boride/nitride composites including $\text{TiB}_2$/TiN and $\text{HfB}_2$/HfN materials were also readily obtained by pyrolysis of metal dispersions in polyborazylene, (B$_3$N$_3$H$_4$)$_x$. The high ceramic yield of metal boride/nitride systems ($\sim$ 98\%) enables their use for the controlled formation of shaped monolithic $\text{TiB}_2$/TiN or $\text{HfB}_2$/HfN materials on pyrolysis. Better results were obtained when polyhexenyldecaborane polymer was used. Boron-containing ceramics, in particular, ceramic fibers were obtained by heat treatment of precursor fibers drawn from decaborane-amine and decaborane-phosphine polymers in inert atmosphere.\textsuperscript{218-221}

### 1.2.3 Polymers derived from vinylpentaborane

2-(Vinylpentaborane) when heated at 125°C gets converted to poly(vinylpentaborane).\textsuperscript{222,223} A crosslinked polymer was obtained when poly(vinylpentaborane) was heated to 140°C, where B-B linkages were formed by
the loss of hydrogen and the crosslinked polymer on pyrolysis in argon at 1200°C gave B₄C in 77% yield.

1.2.4 Polymers derived from boric acid

Wada et al. reported the conversion of borate esters synthesized from boric acid and 1,2,3-propanetriol to ceramics in 1985, though the synthesis and properties of this polymer was reported as early as 1964. A glassy, colorless transparent product was formed which showed spinnability on heating. Pyrolysis of this polymer at 1200°C yielded B₂O₃ regardless of the gas used and duration of heating. When the polymer was heated above 1300°C in nitrogen, BN and B₄C were formed, whereas B₄C was formed when the polymer was heated in argon at 1400°C. The crystallinity of the ceramics increased with increase in heat treatment temperature and heating time. Wada et al. studied the reaction between boric acid and diethanolamine as well as triethanolamine as a means of preparing precursors for BN ceramics. A glassy polymer obtained on pyrolysis under nitrogen at 1400°C gave BN and small amount of B₂C.

Mondal et al. used the borate ester synthesized by condensation of boric acid and triethanolamine to obtain a hard, carbon coating with boron nitride and carbonitride on glass fiber which was used for filtration of molten aluminum. Tian et al. synthesized crystalline hexagonal B(N₁₋ₓCₓ) and cubic B-C-N ceramics from a precursor produced from melamine and boric acid by application of high temperature and high pressure. A low temperature synthetic route for boron carbide was developed by Mondal and Banthia. A polymeric precursor was synthesized by the reaction of boric acid and polyvinylalcohol which on pyrolysis at 400°C and 800°C gave B₄C. X-ray diffraction shows that B₄C obtained by this method has orthorhombic crystal structure.

1.3 Boron and silicon containing polymers

Synthesis of boron and silicon containing polymers has gained importance due to their superior thermo-chemical properties. These polymers on pyrolysis at higher temperatures give non-oxide ceramics such as silicon boride,
SiC-B$_2$C and borosilicon carbonitride. Ceramics derived from boron and silicon containing precursors are found to remain amorphous even up to 2000°C.\textsuperscript{232}

Boron and silicon containing ceramic, when exposed to oxidizing environment at high temperature, forms a protective borosilicate glassy layer on the surface, which prevents further oxidation of the ceramic. Boron and silicon containing polymers are mainly prepared by the following four synthetic methods:

(i) by reacting functional monomers of boron with functional monomers of silicon, (ii) by reacting functional monomers containing both boron and silicon with functional monomers of silicon, (iii) by chemical modification of organosilicon polymers with boron compounds and (iv) through the reaction of single source precursor containing both boron and silicon with suitable comonomers.

1.3.1 From functional monomers of boron with functional monomers of silicon

Borosiloxane oligomers/polymers synthesized from boric acid/borate esters with functional monomers of silicon fall under this category. As the present thesis deals with borosiloxane oligomers, the literature on this topic is dealt with in a separate section.

Synthesis of boron and silicon containing polymers reported by Ricitiello et al.\textsuperscript{233-235} involves the dehalogenation of borontrichloride and dialkyldichlorosilane such as DMDCS or MVDCS in presence or absence of methylidide in hydrocarbon solvents. Gutenberger et al.\textsuperscript{236} synthesized poly(borodiphenylcarbosilane) free of oxygen by reacting DPDCS, dibromomethane and phenyldichloroborane or borontribromide with sodium.

Sundar and Keller\textsuperscript{237} synthesized acetylenic polymers by reacting 1,4-dilithiobutadiyne with phenylboron dichloride and DMDCS. The incorporation of silicon and boron into the diacetylenic polymer was found to enhance the oxidation stability of the polymer. They also reported\textsuperscript{238} the synthesis of borocarbosilicate polymer containing diacetylenic functionalities with improved thermal properties, by reacting DPDCS and 1,4-dilithiobutadiyne with
phenylboronic acid. Boron and silicon containing polymers having acetylinic units in the backbone were also synthesized by reacting bis(dimethylchlorosilyl)benzene with phenylboronic acid.\textsuperscript{239}

1.3.2 From functional monomers of boron and silicon with functional monomers of silicon

Poly(carborane-siloxanes)s synthesized from functional monomers of boron and silicon with functional monomers of silicon represent another class of boron and silicon containing polymers. Poly(carborane-siloxane)s marketed under the trade name "Dexsil" contain carborane units along with siloxane units in the backbone (Structure 8). Dexsil polymers are prepared by the condensation polymerization of bis(methoxydimethylsilyl)-m-carborane with alkylchlorosilane or alkylchlorosiloxane or bis(chlorosilyl)-m-carborane derivatives in presence of a catalyst\textsuperscript{240-245}

\begin{equation}
\begin{array}{c}
\text{CH}_3 \\
\text{SiC}_{10}\text{H}_{10}\text{C} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{Dexsil 100 crystalline polymer}
\end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{SiC}_{10}\text{H}_{10}\text{C} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{Dexsil 200 elastomer}
\end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{SiC}_{10}\text{H}_{10}\text{C} \\
\text{CH}_3 \\
\text{CH}_3 \\
\text{Dexsil 300 elastomer}
\end{array}
\end{equation}

\textbf{Structure 8. Structures of different poly(carborane-siloxane)s}

Dexsil 202 is a viscous liquid and consists of m-carborane cage attached to a dialkyl or diarylsiloxane unit with a small amount of 1-vinyl-o-carbonyl side group to enhance the crosslinking. Dexsil polymer serves as a precursor for boron and silicon containing ceramics.\textsuperscript{246,247} The incorporation of carborane units prevents the degradation of polysiloxanes by ring forming depolymerization and
enhances the resistivity towards high temperature degradation particularly in inert atmosphere. Pyrolysis of these polymers in nitrogen atmosphere led to the degradation of carborane cage at around 700°C leaving an amorphous borosiliconoxycarbide (BSiOC), which got converted to β-SiC and B$_4$C on further heating to 1300°C by the carbothermal reduction of BSiOC phase.

A highly functionalized carborane-siloxane polymer was synthesized by Kulig et al.$^{248}$ from 1,7-bis(hydroxydimethylsilyl)-m-carborane and methyltriacetoxy-silane. The polymer formed has one acetoxy crosslinking site per repeat unit. This polymer has a molecular weight of 6,000 and is soluble in THF and toluene. This polymer was evaluated as an AO resistant coating for low earth orbit space structures.$^{248,249}$

### 1.3.3 Chemical modification of organosilicon polymers

Niebylski$^{250,251}$ synthesized organoborosilazane polymers by reacting trialkoxy, triaryloxy or tri(arylalkoxy)boroxine with polysilazane. Chemical modification of hydridopolysilazane was performed by reacting it with liquid borazine at low temperatures to obtain boron and silicon containing polymers.$^{252,253}$ Chemical modification of hydridopolysilazanes with monofunctional boranes such as pinacolborane (Me$_2$CO)$_2$BH, 1,3-dimethyl-1,3-diaza-2-borocyclopentane (CH$_2$NMe)$_2$BH and 2,4-diethylborazine (Et$_2$B$_3$N$_3$H$_4$) has also been reported.$^{254}$

Chemical modification of silazanes with borane-dimethylsulfide was studied by Seyferth et al.$^{255}$ In this method oligomeric silazane (CH$_3$SiHNH)$_n$ was treated with BH$_3$.S(CH$_3$)$_2$ to obtain a crosslinked polyborosilazane. The polymer obtained as a low melting white solid has molecular weight of 800. Polyborosilazane was also derived from perhydropolysilazane and trimethylborate.$^{256}$ Polyborosilazane with low oxygen content was synthesized by reacting perhydrosilazane with tris(dimethylamino)borane.$^{257}$

The synthesis and thermal behavior of boron-modified polysilazanes [B(C$_2$H$_4$Si(R)NH)$_3$]$_n$ and polysilylcarbodiimides [B[C$_2$H$_4$Si(R)NCN]$_3$]$_n$ were reported by Aldinger and Weinmann (Scheme 1.8).$^{258}$
These Si-B-C-N ceramic precursors were obtained by treating vinyl substituted polysilylcarbodiimides \([\left(\text{H}_2\text{C}=\text{CH}\right)(\text{R})\text{SiNCN}]_n\) with borane-dimethylsulfide \(\text{BH}_3\cdot\text{S}((\text{CH}_3)_2)\). The polysilylcarbodiimides themselves were synthesized via treatment of vinyl-substituted chlorosilanes \((\text{H}_2\text{C}=\text{CH})(\text{R})\text{SiCl}_2\) with cyanamide, \(\text{H}_2\text{N}-\text{C}≡\text{N}\), in the presence of pyridine, or via the reaction of the vinyl-substituted chlorosilanes with bis(trimethylsilyl)carbodiimide, \((\text{H}_3\text{C})_3\text{SiN}≡\text{C}≡\text{N}-\text{Si}((\text{CH}_3)_3)\). Alternatively, these compounds were synthesized via hydroboration of vinyl-substituted chlorosilanes with borane-dimethylsulphide, borane-trimethyl-amide or borane-triethylanhydride yielding tris[(chlorosilyl)ethyl]boranes initially.

The synthesis by a novel reaction pathway and the polymer-to-ceramic conversion of boron-containing polysilylcarbodiimides were reported by Weinmann et al.\textsuperscript{155,259} Polysilylcarbodiimides were prepared by reaction of tris(hydridosilylethyl)boranes with different amounts of cyanamide in THF.
Thermolysis of such compounds in an argon atmosphere delivers Si-B-C-N ceramics in 65-85% yield.

Polysilazanes with polymerizable pendant groups were synthesized by Weinmann et al.\textsuperscript{260} These pendant groups enable crosslinking thereby minimizing depolymerization during ceramization.

A new kind of polyborosilazane was synthesized by Zeng et al.\textsuperscript{261} from hexamethylcyclotrisilazane by exposure to borontrichloride. It was observed that the boron content of the precursor increased as the exposure time was increased whereas the C/Si ratio remained constant. The pyrolysis of the precursor was carried out at 1250°C, 1600°C and 1800°C in nitrogen. Heat treatment of the polymer at 1800°C resulted in BN crystals.

Schiavon et al.\textsuperscript{262,263} synthesized poly(borosilazanes) with Si/B molar ratios of 3 and 9, via hydroboration, of vinyl-substituted cyclotrisilazane, [CH\textsubscript{2}=CH(CH\textsubscript{3})\text{SiNH}]\textsubscript{3}, with borane-trimethylamine adduct, BH\textsubscript{3}.N(CH\textsubscript{3})\textsubscript{3}. The polyborosilazanes were pyrolyzed up to 1000°C under argon atmosphere, which resulted in amorphous silicon boron carbonitride (SiBCN) glasses. The SiBCN glass with B/Si= 3 was amorphous up to 1700°C and at this temperature, β-SiC and β-Si\textsubscript{3}N\textsubscript{4} were formed. At 2000°C, β-SiC and BN were formed. These ceramics have a number of advantages when compared to the corresponding B-free Si-C-N system, which include higher thermal stability, oxidation resistance, crystallization temperature and ceramic yield.

1.3.4 From single source precursors

Baldus et al.\textsuperscript{264,265} synthesized polyborosilazane by reacting a single source precursor, viz., chlorosilylamidchloroborane [Cl\textsubscript{3}Si-NH-BCl\textsubscript{3}] with methylamine to obtain a processable polymer in 80% yield. The polyborosilazane consists of [Si\textsubscript{3}NCH\textsubscript{3}]\textsubscript{3} six membered ring connected via. HN-B- and -N(CH\textsubscript{3})-B-units respectively. This polymer has an average molecular weight of 2,500 and melts at 140°C. Prolonged heating at temperatures above 180°C caused further crosslinking and the polymer became infusible. Pyrolysis of this polymer in argon or nitrogen at 1650°C led to the formation of amorphous borosiliconcarbonitride
[Si-B-N-C] ceramic in 70% yield and the ceramic obtained did not crystallize on heating in nitrogen up to 1900°C. This polymer was also used for coating and for infiltration of woven carbon fibers, carbon fiber composites and porous ceramic materials.\textsuperscript{265}

Rieder\textsuperscript{266} explored the hydroboration of MVDCS with borane-dimethylsulfide \([\text{(CH}_3\text{)}_2\text{S.BH}_3]\). Addition of \((\text{CH}_3\text{)}_2\text{S.BH}_3\) to MVDCS in toluene resulted in the formation of a precursor \text{tris(dichloromethylsilylethyl)borane}. This organosilylboron was subsequently polycondensed with ammonia at 0°C in tetrahydrod furan to obtain a polyorganoborosilazane in 80% yield. Pyrolysis of this polymer in argon at 1000°C resulted in the formation of SiBCN ceramic in 62% yield. The crystallization of this ceramic commenced at 1700°C and the crystallization was completed above 2000°C.

The requirement of high pyrolysis temperature for carbothermal reduction of silicon oxide components has led to the development of oxygen free carborane-silicon compounds. Zheng et al.\textsuperscript{247} synthesized several oxygen free boron and silicon containing monomers. These molecules were volatile compounds due to their low molecular weight.

The high temperature properties of poly(carborane-siloxane)s were improved by incorporating acetylinic units in the polymer backbone. Henderson and Keller\textsuperscript{267,268} synthesized poly(carborane-siloxane-acetylene) polymers by reacting equal amount of 1,4-dilithiobutadiyne and 1,7-bis(chlorotetramethyl-disiloxane)-m-carborane. A linear polymer soluble in common organic solvents and having molecular weight \(\overline{M}_w\) of 4,900 was obtained in 97% yield.

The incorporation of acetylinic units in the polymer backbone has the added advantage that they remain dormant during ambient temperatures, but can be used for crosslinking at higher temperatures. The linear poly(carborane-siloxane-acetylene) can be readily converted to a thermoset by thermal crosslinking, where additional polymerization reaction occurs with out the formation of volatile by-products. Pyrolysis of this polymer yielded a black solid ceramic in 85% yield.
Bucca and Keller\textsuperscript{269} investigated the possibility of incorporating boron and silicon in arylacetylenic compounds. These monomers can be converted to thermally stable thermosets, which on pyrolysis give ceramic like materials. When these materials were exposed to oxidizing environment at elevated temperatures protective inorganic oxides were formed on the surface. These inorganic oxide layers act as a barrier to protect the interior from degradation. Of late, they reported\textsuperscript{270} that boron and silicon containing acetylinic monomer viz., 1,7-bis(4-phenylethylphenyltetramethyl-disiloxyl)-m-carborane can be copolymerized with 1,2,4,5-tetrakis(phenylethynyl)-benzene to obtain thermosets and chars having outstanding thermooxidative properties.

Jansen and Kroschel\textsuperscript{271} synthesized an amorphous ceramic, SiBNC, obtained from 1,1-dichloro-N-(trichlorosilyl)boraneamine and N-methyl polyborosilazane. The pyrolysis proceeds in three clearly divided steps, which can be assigned to completion of the polycondensation (200-350°C), fragmentation (580-620°C) and elimination of residual hydrogen (1000-1300°C).

1.4 Polyborosiloxanes

Polysiloxanes undergo degradation by forming cyclics by back-biting mechanism. This problem has been overcome through the incorporation of borosiloxane and metallosiloxane linkages. Polyborosiloxanes have been an exploration target because of their thermodynamically stable backbone linkage, despite their high susceptibility to hydrolysis. They cannot be used themselves as high temperature polymers but show interesting properties and can be used as precursors for ceramic binders, additives and coatings. They are also investigated in sol-gel chemistry as precursor sols and/or as precursors for borosilicate glasses. Several methods have been described for the synthesis of polymers containing -Si-O-B-O-linkages using di- and trifunctional silicon compounds\textsuperscript{272,273} as the source of silicon, and boric acid, borontrioxide, borontrichloride, boron tribromide and borate esters as the source of boron. The literature on borosiloxanes is presented in this thesis under the following four categories: (i) borosiloxanes from boric acid, (ii) borosiloxanes from borate esters, (iii) sol-gel process and (iv) organically modified SiO\textsubscript{2}-B\textsubscript{2}O\textsubscript{3} gels.
1.4.1 Borosiloxanes from boric acid

Boric acid reacts with chlorosilane, alkoxy silane or silanol as shown below resulting in the formation of borosiloxane linkage.\textsuperscript{274, 275}

\[
\begin{align*}
3R_3SiCl + B(OH)_3 & \rightarrow (R_3SiO)_3B + 3HCl \\
3R_3SiOR' + B(OH)_3 & \rightarrow (R_3SiO)_3B + 3R'O\text{H} \\
3R_3SiOH + B(OH)_3 & \rightarrow (R_3SiO)_3B + 3H_2O
\end{align*}
\]

Dimethyl diethoxysilane reacts with boric acid to give viscous liquid soluble in organic solvents. When methyl triethoxysilane is used, infusible and insoluble solids are formed. Polyborosiloxanes obtained by the reaction of boric acid with diethyl diethoxysilane are more stable to hydrolysis. In these cases, the side reaction to form triethoxyborane is controlled.

Ambadas et al.\textsuperscript{276} prepared borosiloxane oligomers through the condensation of boric acid with PTMOS and VTEOS in diglyme at 150-160°C. These oligomers give ceramic residue in the range of 68-85%. Borosiloxane oligomer containing vinyl group gives higher ceramic residue compared to the one containing phenyl group and this is attributed to the crosslinking of vinyl groups. Yajima et al.\textsuperscript{273} synthesized poly(borodiphenylsiloxane) by reacting boric acid with DPDCS in n-butylether under nitrogen atmosphere for 18 h at 300°C (Scheme 1.9).

The above polymer was obtained in 92% yield and found to be far more moisture resistant than its analog prepared from boric acid and DMDCS. Poly(borodiphenylsiloxane) softens at 100°C and is stable up to 500°C when heated in air. The use of this polymer as a catalyst for the thermal conversion of PDMS to polycarbosilane has been discussed in the section on polysilanes.
Kobayashi\textsuperscript{277} reported the preparation of borodiphenylsiloxanol by the condensation reaction of boric acid and diphenylsilanediol and then polycondensing the borodiphenylsiloxanol to obtain borosiloxanes with $\bar{M}_n$ ranging from 800-5000.

Hoshii et al.\textsuperscript{278-280} synthesized borodiphenylsiloxane oligomers by reacting diphenylsilanediol with boric acid (in different mole ratios) at 300°C in nitrogen atmosphere in presence of dibutylether and N-methyl-2-pyrrolidone. The oligomers have molecular weight ($\bar{M}_n$) in the range of 510 to 610 and gave a ceramic residue of 59-70% when pyrolyzed at 1000°C.

1.4.2 Polymers from borate esters

Among the borate esters tris(trialkylsiloxy)boranes, (R$_3$SiO)$_3$B (R= Me, Et) and bis(tri-t-butoxysiloxy)-n-butoxyborane have been reported as model compounds for preparation of polyborosiloxanes.\textsuperscript{274} The reaction of chlorosilanes or silanols with trialkoxyboranes\textsuperscript{277} results in the formation of polyborosiloxanes.

Partially hydrolyzed tetraethoxysilane reacts with trialkoxyborane, followed by further hydrolytic polycondensation to give borosilicate via sols and borosiloxane gels.\textsuperscript{281}

Since polyborosiloxanes formed in a sol-gel process are unstable and could not be isolated, heterofunctional polycondensation of tetraacetoxy silane and tri-n-butoxyborane has been investigated to prepare and characterize the polymers.\textsuperscript{281} The reaction provides only a low molecular weight polymer ($\bar{M}_n = 300-400$). However, polyborosiloxanes of $\bar{M}_n$ more than 5000 (HPBS), which show good spinnability, were obtained by controlled alkoxylation, followed by partial hydrolysis and final condensation in a sealed flask (Scheme 1.10). Dry spinning of polymers (HPBS) provides SiO$_2$-B$_2$O$_3$ precursor fibers.\textsuperscript{282}

\begin{equation}
\begin{align*}
\text{Si(OAc)}_4 + \text{B(OBu)}_3 & \xrightarrow{\text{THF Reflux}} \text{BS} \xrightarrow{\text{Alkoxylation with EtOH}} \text{PBS} \\
\text{TAS} & \xrightarrow{\text{Partial hydrolysis}} \xrightarrow{\text{Condensation/60 C}} \text{HPBS}
\end{align*}
\end{equation}

Scheme 1.10. Preparation of polyborosiloxanes and/or SiO$_2$-B$_2$O$_3$ gels
Polyborosiloxanes and gel fibers were more easily prepared by reacting silicic acid and tributylborate in various molar ratios as shown in Scheme 1.11. The solution was concentrated in vacuum and then allowed to stand in a sealed flask at room temperature or at 60°C for a certain time to form a viscous solution from which gel fibers could be drawn just before gelation.

Scheme 1.11. Preparation of polyborosiloxanes from silicic acid

Beckett et al.\textsuperscript{283} reported the synthesis of alkali-free borosilicate gel from Si(OEt)\textsubscript{4} and (MeO)\textsubscript{3}B\textsubscript{3}O\textsubscript{3} in non-aqueous solvents. The formation of the gel proceeds via rapid transesterification/oxygen transfer with elimination of B(OR)\textsubscript{3} followed by removal of volatiles from the gel and then drying at 60°C and subsequent heating in air at 600°C resulted in alkali-free borosilicate glass.

Synthesis of borosiloxanes through the reaction of borontrialkoxide with dialkyldiacetoxyisilane or tetraacetoxyisilane was reported by Kasgoz et al.\textsuperscript{284,285} These polymers were investigated as precursors for preparation of homogeneous borosiloxane gels.

Pillot et al.\textsuperscript{286} prepared polyborosiloxanes by the condensation of polychlorosilane and an alkylborate, B(OR)\textsubscript{3}, in presence of a catalyst. This polymer on nitridation followed by pyrolysis gave crystalline boron and silicon oxynitride ceramics.

1.4.3 Sol-gel process

It involves the preparative techniques heavily based on chemical reactions, for example, the generation of ceramic type materials by the hydrolysis of an organometallic compound. The sol-gel name applied to this approach comes
from the fact that, in at least some of these synthesis, a dispersion of particles
called a sol is produced and these particles can aggregate into gels as
intermediates to final ceramic like materials. The most important reaction of this
type involves the catalytic hydrolysis of tetraethoxysilane (TEOS).\textsuperscript{287} Hydrolysis
and condensation reactions in an anhydrous sol-gel system comprising TEOS,
boric acid and ethanol were studied by Zha et al.\textsuperscript{288} Boric acid is able to hydrolyse
TEOS directly, and subsequent condensation reactions form borosiloxane and
siloxane linkages whereas in an aqueous system, borosiloxanes are unstable to
hydrolysis and are formed only upon heat treatment of the gel. The anhydrous
mixture is stable indefinitely against gelation, but can be readily gelled by addition
of NaOH in ethanol and this system is useful for preparing borosilicate glasses at
lower temperatures with good homogeneity.

Borophosphosilicate glass–ceramics has been synthesized by Li et al.\textsuperscript{289}
by sol–gel process using boric acid, phosphoric acid and TEOS as starting
precursors. The borophosphosilicate glass–ceramics can be sintered below 950°C
in air. It was found that the SiO\textsubscript{2} glass phase wraps up BPO\textsubscript{4} crystallites and
Si\textsubscript{3}(PO\textsubscript{4})\textsubscript{4} crystallites exist when the SiO\textsubscript{2} content is decreased. The glass
ceramics show good potential as dielectric materials in super high frequency multi-
layer chip inductors (MLCI).

Different precursors were synthesized through the sol-gel process using
tetraethoxysilane, triethylborate and polydimethylsiloxane by polycondensation
between the Si(OH)\textsubscript{3} groups from the hydrolyzed tetraethoxysilane and the
polydimethylsiloxane.\textsuperscript{290} Mixed vitreous oxycarbide glasses containing silicon and
boron were prepared by pyrolysis of the hybrid precursors in nitrogen at 1100°C.
The spectral studies indicate that boron is not incorporated into the network until
pyrolysis of the precursors that form the oxycarbides. The oxycarbides were
porous made of spherical interconnected particles and the porosity and mean pore
size of the glasses increased with increase in triethylborate content.

Sodium silicate solutions were mixed with boric acid in order to form
sodium borosilicate gels and the gelation process was studied by Boschel and
Roggendorf.\textsuperscript{291} The effect of composition and temperature on the gel point was
studied in detail.
A patent literature discloses a process for the borosilicate glass formation. Silicon tetraalkoxide and borate ester were combined with water in excess of that required for hydrolysis of alkoxide groups and the alkanol and water formed were removed by fractional distillation from the reaction product to obtain borosilicate glass.

### 1.4.4 Organically modified SiO$_2$-B$_2$O$_3$ gels

Preparation of binary SiO$_2$-B$_2$O$_3$ gels as precursor for borosilicate glasses has been reported by several authors using sol-gel process. Sol-gel process was chosen with the aim of preparing, via cocondensation reactions between TEOS and triethylborate or boric acid, a more homogenous network compared to the traditional melting route.

SiO$_2$-B$_2$O$_3$ gels, have been extensively studied as precursors for borosilicates or oxynitride glasses. It is found that the boron atoms are present in the silica matrix as a separate B$_2$O$_3$ and/or B(OH)$_3$ phase. This is probably due to the well known reactivity of the B-O-Si bonds towards hydrolysis. The borosiloxane linkages that might form in the early stages of the sol-gel process are consumed at the end when increasing amount of water is produced via condensation. Soraru et al. have recently shown that if a modified silicon alkoxide, such as RSi(OEt)$_3$, where R = Me, Et or Vi is cohydrolyzed with tetraethylborate, then a large amount of trigonal BO$_3$ units are incorporated in the hybrid siloxane-network via B-O-Si bridges, leading to borosiloxane gels. The resulting gels appear homogeneous, clear and no evidence of the formation of a crystalline B(OH)$_3$ can be detected. The retention of B-O-Si bonds in the hybrid borosilicate gels is partly due to: (i) the low hydrolysis ratio used in the sol-gel synthesis ($H_2O$/Si = 1.5), (ii) the in situ protection that the hydrophobic organic groups bonded to silicon provide against water attack and (iii) the higher electron density at the silicon atoms in the organically substituted gels which strengthen the Si-O bonds.

In a modification of the above approach, the production of homogenous borosilicate gels were tried by a new process in which the modified silicon
alkoxides are directly reacted with boric acid without any external addition of water. Here the hybrid borosilicate gels were synthesized according to a new route, by adding boric acid to the liquid silicon alkoxide and by stirring until its complete dissolution. The clear solutions were then cast in plastic test tubes that were left open for gelation. Wet gels were dried for at least 10 days at 60°C. ¹¹B-MAS NMR spectroscopic studies showed the formation of homogeneous borosilicate gels and the incorporation of boron atoms into the siloxane network via B-O-Si bridges. On the other hand, when a conventional tetrafunctional silicon alkoxide such as TMOS or TEOS is reacted with boric acid the expected borosilicate gels are not formed. The homogeneous borosilicate, obtained from boric acid and alkoxysilanes, on pyrolysis results in the formation of homogeneous amorphous borosilicon oxycarbide (BSiOC) glasses.

The structural conversion of silicate gel to glass was investigated by Yang and Woo in the temperature range of 150-850°C by using solid-state ¹H- and ²⁹Si-NMR spectroscopy. The conversion process is continuous and dependent on the stabilization temperature. The silicate gel to glass conversion process is completed at 850°C. The incorporation of boron in silicate backbone provides the formation of ≡Si-O-B= bonds which results in the formation of borosilicate gels.

1.4.5 Applications of borosiloxanes

The end uses of preceramic polymers are dealt in detail in next section. As the present thesis deals mainly with borosiloxane oligomers, specific end uses of polyborosiloxanes are dealt in some detail in this sub section.

Polyborosiloxanes find end-uses as catalysts for the conversion of polydimethylsilane to polycarbosilane, binders for making SiC components and precursors for SiC-BₓC ceramics and thermal protection coatings. Polyborosiloxanes synthesized by sol-gel process, are used for preparing borosilicate bulk bodies, powders, thin films and fibers with high purity and molecular homogeneity under mild conditions. Borosilicates are known to be especially useful as cladding material for wave guides. Since they have a lower refractive index than pure fused silica, low attenuation in glass fibers is more
Introduction

They have also been used as passivation layers for microelectronic devices and as heat-resistant inorganic fibers. Polyborosiloxanes serve as binders, coatings and heat-resistant paints for far infrared ray irradiators, exhaust systems of cars and electric wires. A metal plate can be coated to a thickness of 5 µm with a polyborosiloxane layer containing metal oxides to form a solar collector. Polyborosiloxane find wide variety of end-uses such as adhesive for joining two substrates, curing agents for epoxy resins, and as heat curable polymers.

1.5 End uses of preceramic polymers

Preceramic polymers find wide range of applications as high temperature polymers, high temperature rubbers, thermal protection systems, and oxidation resistant coatings, matrix resins for ceramic matrix composites, precursors for ceramic fibers, binders for making ceramic components and precursors for obtaining ultra-fine ceramic powders. End-uses of some of the preceramic polymers whose synthesis were dealt with in the preceding sections are discussed in this section.

1.5.1 Protective coatings

Organometallic polymers find application as protective coatings for a variety of substrates including carbon/carbon composites, carbon/graphite fibers, ceramic fibers, ceramic matrix composites, metals and metal oxides. Protective coatings derived from organometallic polymers offer potential
advantages over the conventional methods. The advantages include short processing time, processing flexibility, ability to form coating on complex shaped objects, processing at low temperature enabling ceramic formation under milder conditions, high purity of the final ceramic, precise control of ceramic composition, ability to apply multiple coating with relative ease and tailoring the coating chemistry to obtain desired properties. A detailed discussion on various preceramic polymer systems used as coatings is made in chapter 3.5.

Besides their end-uses as high temperature resistant materials, precursors for ceramics and oxidation resistant coatings for carbon-based substrates, inorganic and organometallic polymers find utility as atomic oxygen (AO) resistant coatings for low earth orbit (LEO) space structures. A comprehensive account of different polymeric systems used as AO resistant coatings is given in Chapter 3.7.

1.5.2 Ceramic fibers

Preparation of ceramic fibers from organosilicon polymers was first reported by Yajima et al. SiC fiber was obtained by a process which starts from DMDCS and involves the synthesis of polysilane and its conversion to polycarbosilane by heat treating it in an inert atmosphere under pressure around 450°C or in presence of borodiphenylsiloxane catalyst at 350°C. Green fibers (10-20 µm diameter) were obtained by melt spinning the precursor. They were made infusible by surface oxidation and then subjected to pyrolysis at 1400°C to get SiC fibers. The presence of oxygen in the final ceramic fibers is a drawback associated with this process.

Silicon carbide fibers with low oxygen content (<2%) were prepared by suitably modifying the spinning or curing process of green fibers followed by pyrolysis. SiC fiber with low oxygen content was also obtained by pyrolyzing the green fibers drawn from a blend of polycarbosilane and hydroxy-terminated polybutadiene. Hasegawa and Okamura observed that the incorporation of hetero atoms such as titanium, zirconium or vanadium into the precursor polymer
enhanced the thermal stability of the ceramic fibers formed. Meyer et al. explored the use of silylene-acetylene polymer as a precursor for preparing SiC fibers. Preparation of silicon oxynitride fibers by pyrolysis of polycarbosilane fibers in ammonia and silicon carbonitride fibers by pyrolysis of polysilazane fibers in inert atmosphere were reported. Silicon nitride ceramic fibers were also prepared by heating the polymeric fibers derived from perhydropolysilazane.

Various other preceramic polymers have been prepared and evaluated as precursors for SiC fibers. Fibers made of SiBNC were derived from a single source precursor, \( \text{Cl}_2\text{Si(NH)BCl}_2 \) and it retained the mechanical strength, as measured by creep resistance and tensile strength, up to 1400°C. A variety of borylborazine-based polymers were successfully converted into BN fibers via the preceramic polymer route. Recently, Sneddon et al. developed new decaborane-based polymeric precursors to B,C nanofibers.

### 1.5.3 Binders for ceramics

Current techniques of preparing ceramic components are based on pressureless sintering of green body. The major drawback associated with this process is that the voids often remain in the final structure and these voids have a deleterious effect on the structural properties of ceramic. When preceramic polymer is used for making green body, the void that would have formed during organic binder burn-out would be replaced by a polymer-derived ceramic. The first reported literature in this field was by Yajima et al. where a three dimensional polycarbosilane was used as a binder for SiC sintered bodies. Following this invention, Yajima et al. studied borodiphenylsiloxyxane as binders for SiC and Si,N4 sintered bodies. Polysilastrene was used as a binder for making SiC components from \( \beta \)-SiC powder, and polycarbosilane and polysilazane were used as binders for making injection moulded silicon nitride parts. Sawai et al. reported that the compaction of SiC ceramic was improved when polycarbosilane containing organofluoric groups was used as a binder.
1.5.4 Matrix resins for CMC

CMCs are tough materials and show a high failure stress when the fiber-matrix bonding is either too strong or too weak. The bonding strength is usually obtained through the use of the fiber coating referred to as the interphase. CMCs are used as thermostructural materials under severe service conditions like high temperatures under load and in corrosive atmospheres. The most common CMCs used are non-oxide CMCs mainly C-SiC and SiC-SiC, the fibers being specified first. There are three constituents in a CMC, which are the reinforcement, a matrix and generally an interphase. The nature, volume fraction and arrangement of the constituents depend on a number of factors including the function of the part to be fabricated, the service conditions and the cost.

Ceramics by themselves have low fracture toughness and they fail catastrophically. Reinforcing them with fibers increase their fracture toughness thereby preventing catastrophic failure of the composite. Incorporation of fibers, whiskers or particles into a ceramic matrix can result in a tough material. The introduction of the reinforcement into the matrix results in energy-dissipating phenomenon such as debonding at the fiber-matrix interface, crack deflection, fiber bridging and fiber pullout. In this regard, proper control of the interface region characteristics assumes great importance. The ratio of the moduli of the reinforcement to that of the matrix is generally between 10-100 for a polymer or metal matrix composite, while for CMC it can frequently be equal to or lower than unity. The high ratio in polymer or metal matrix composites allows an efficient load transfer from the matrix to the fibers through the strong interface. In a CMC, the low modulus ratio infers that the fibers and the matrix are not much different in their load bearing capacity. Thus, the role of the fiber reinforcement is to enhance the toughness and strength of the composite by bridging the matrix cracks. This requires a relatively weak interphase between the matrix and the fibers, so that the matrix cracks induce interfacial debonding rather than failure of the fiber as the cracks traverse the specimen’s cross-section. Accordingly, the interphase has a key role in CMC even though its volume fraction is extremely low. This thin coating which is deposited on fibers or formed in situ during composite processing serves the functions of load transfer, crack deflection and diffusion barrier in reactive fiber
Introduction

The best interphase materials are pyrocarbon (PyC), hexagonal BN or a layered microstructure like (SiC-PyC)_m. The interphase coatings are usually obtained by CVD process using suitable gases. Of late, preceramic polymers are also used for getting interphase coatings. CMCs can be processed either by conventional powder processing techniques used for processing polycrystalline ceramics such as cold pressing and sintering, hot pressing and reaction bonding or by newer techniques such as infiltration, chemical vapor infiltration (CVI), sol-gel process and polymer impregnation and pyrolysis.

Among these methods the most widely used one is the polymer infiltration and pyrolysis. Because of the generally high cost of processing CMCs, polymer infiltration is an attractive processing route due to its relatively low cost. This approach allows near-net-shape molding and fabrication technology that is able to produce nearly fully dense composites. Here, the fibers are infiltrated with an organic polymer, which is heated to fairly high temperatures and pyrolyzed to form a ceramic matrix. Due to the relatively low yield of polymer to ceramic, multiple infiltrations are used to densify the composite. Polymeric precursors for ceramic matrices allow one to use conventional polymer composite fabrication technology that is readily available and to take advantage of processes used to make polymer-matrix composites. By processing and pyrolyzing at lower temperatures (compared to sintering and hot pressing) one can avoid fiber degradation and the formation of unwanted reaction products at the fiber/matrix interface. A detailed discussion on this topic is made in chapter 3.5.

1.5.5 Ceramic foam

There is considerable interest shown on ceramic foams which possess a number of favorable properties such as low density, low thermal conductivity, thermal stability, high specific strength and high resistance to chemical attack and are suitable for industrial applications such as high temperature thermal insulation, hot gas particulate filters, hot metal filters, catalyst supports and cores in high temperature structural panels. The following processing routes have been reported for the preparation of ceramic foams: (i) direct foaming of ceramic slurries, sol-gel solutions or preceramic polymers (ii) chemical vapour deposition.
of various refractory materials on foamed carbon skeletons\textsuperscript{373} (iii) sintering of hollow spheres\textsuperscript{374} and (iv) replication of polyurethane foam with ceramic slurries.\textsuperscript{375} Of these methods, the first and the fourth one are mostly used for making ceramic foams.

1.6 Objective and scope of the present investigation

The survey of pertinent literature on preceramic polymers presented above reveals that the interest on these speciality polymers is ever growing. This trend is attributed to their potential application as precursors for ceramic fibers, ceramic coatings and ceramic foams, binders for ceramics and matrix resins for ceramic matrix composites. Though a large amount of work has already been done in the area of preceramic polymers and their applications, there still exists enormous scope for developing cost effective synthetic approaches for the preparation of novel precursors for ceramics, capable of giving high ceramic residue. Thus, the present investigation envisages to synthesize certain speciality oligomers/polymers containing silicon and both silicon and boron and evaluate them as precursors for ceramics.

Among the preceramic polymers boron and silicon containing polymers/oligomers have gained importance as they offer certain advantages when compared to polymers which contain only boron or silicon. The ceramics derived from such polymers remain amorphous even at temperatures exceeding $1500^\circ C$ and hence, have better mechanical properties at these temperatures compared to simple non-oxide ceramics which undergo extensive crystallization. While several synthetic approaches are reported for the preparation of boron and silicon containing preceramic polymers, cost effective and simple method to prepare these polymers is by alkoxysilanes with boric acid, a cheap source of boron. Though considerable literature is available on the synthesis of borosiloxanes by sol-gel process there appears to be very limited information on the synthesis of these polymers by non-aqueous sol-gel process. Thus, the main objective of the present investigation is to synthesize novel borosiloxane oligomers by non-aqueous sol-gel process, evaluate them as precursors for ceramics and study their end-uses for space applications.
While designing a preceramic oligomer/polymer, one should bear in mind that it should be processable, i.e., soluble in organic solvents and/or meltable and should give ceramic residue in high yield. To achieve this objective, it is required to carry out a systematic investigation on the synthesis of borosiloxanes by using different alkoxysilanes, varying the monomer feed ratios and experimental conditions. To begin with attention has been focused on synthesizing borosiloxane oligomers by reacting boric acid with phenyltrimethoxysilane (PTMOS) and phenyltriethoxysilane (PTEOS). As PTEOS is much cheaper than PTMOS emphasis has been laid on synthesizing borosiloxane oligomers from the former.

Synthesis of borosiloxane oligomer from boric acid and vinyltriethoxysilane (VTEOS) has been reported by Ambadas. The choice of VTEOS is justified from the fact that vinyl group present in the oligomer would undergo crosslinking and hence would give high ceramic residue. The oligomer synthesized from VTEOS is reported to give a ceramic residue of ~85% at 900°C in inert atmosphere. However, a detailed study on the effect of monomer feed ratio on the thermal stability and ceramic residue has not been reported. Thus, in the present investigation attention has been focused on this aspect. As the presence of vinylsiloxy units is expected to improve the ceramic residue, it would be of interest to study the feasibility of synthesizing borosiloxane oligomers using a mixture of VTEOS with other alkoxysilanes. The advantage of this approach is that processable borosiloxane oligomers with improved ceramic residue can be obtained. A detailed study has therefore been undertaken to synthesize borosiloxane oligomers using mixtures of VTEOS with PTEOS and PTMOS.

Epoxy resins have gained significance due to their versatility and they find extensive application as adhesives, matrix resins, potting compounds and coating. Considerable amount of work has been done on epoxy-functionalized siloxane resins. However, there is very little information on borosiloxanes containing epoxy functional group. The advantage of such a resin is that unlike vinyl-functionalized borosiloxanes which require high temperatures (above 150°C) for curing, epoxy functionalized borosiloxanes can be cured at room temperature. This advantage can be exploited for infiltrating porous ceramic matrix composites (CMCs) and then curing the infiltrated resin thereby preventing the resin ooze-out from the
composite. Keeping in view of this, in the present work efforts have been directed towards preparing epoxy-functionalized borosiloxane oligomers by reacting boric acid with glycidoxypropyltrimethoxysilane (GPTMOS). As GPTMOS contains aliphatic linkages, it is expected that the overall thermal stability and ceramic residue of such oligomers would be lower than the ones synthesized from other alkoxysilanes. This disadvantage could probably be overcome by incorporating vinylsiloxy units in addition to the epoxy functional group. In view of this, borosiloxane oligomers have been synthesized using different mole ratios of boric acid, VTEOS and GPTMOS and characterized.

Besides other end-uses borosiloxanes are also useful as precursors for glass coating. Such glass coatings are expected to find application as overlay coating to seal the cracks in SiC coating applied to C-C composite. For this purpose it is desirable to synthesize borosiloxane oligomers devoid of carbon. If this is difficult to achieve, then the oligomers are to be designed in such a way that the organic groups should be knocked off completely during pyrolysis much before the formation of glass. To achieve this objective borosiloxane oligomer has to be synthesized by reacting boric acid with alkoxysilane having no organic substituents. One such monomer is tetraethoxysilane (TEOS). When boric acid is reacted with TEOS, ethanol would be formed as a by-product and hence the product obtained should contain only B, Si and O. If some unreacted ethoxy group is present it is likely to be knocked off well before 1000°C. In the present investigation, attempts have been made to synthesize borosiloxane oligomers by reacting boric acid with TEOS.

For the synthesis of borosiloxane oligomers, diglyme or 1,4-dioxane has been used as solvent. As they are high boiling solvents, it becomes difficult to remove them and quite often the oligomers undergo gelation while attempting to remove the solvents. Thus, it would be advantageous to synthesize borosiloxane oligomers, particularly the functionalized ones, by solventless process. In this approach, boric acid and alkoxysilane would be reacted directly without using any solvent. The by-product, alkyl alcohol, formed by the reaction of B-OH and -OR would serve as solvent for the reaction. The advantage of the solventless process is that the viscosity and the molecular weight of the product obtained can be
controlled by controlling the amount of alkyl alcohol distilled out from the reaction mixture. Yet another advantage is that the resin synthesized can be directly used for infiltration without any further processing. As alkyl alcohol is low boiling, it can be removed easily. In view of these advantages, attempts have been made to synthesize borosiloxane oligomers, particularly vinyl- and epoxy-functionalized ones, by reacting boric acid with alkoxysilanes without using any solvent.

As discussed earlier, borosiloxane oligomers are expected to have better thermooxidative stability compared to other preceramic polymers. Prior to finding out suitable end-uses of borosiloxane oligomers, it is imperative to study their ceramic conversion. In the present study, selective systems have been subjected to pyrolysis at 900°C followed by sintering at 1400 and 1600°C. The ceramic conversion studies gain significance due to the fact that the presence of boron is expected to suppress the crystallization or in other words increase the crystallization temperature. Borosiloxane oligomers synthesized from boric acid are expected to have 2-6% boron and so it would be interesting to find out the effect of increasing the boron content in borosiloxane oligomers. This can be achieved only by using caged boron compounds. For this purpose, an oligomer containing higher boron content has been synthesized by reacting decaborane(14) with 3-aminopropylmethyldiethoxysilane followed by reaction with boric acid. The ceramic conversion studies of this oligomer have been carried out.

In the present investigation, the possibility of using borosiloxane oligomers as oxidation resistant coatings for carbon-carbon (C/C) composites, precursors for high temperature glass coating and matrix resin for carbon fiber reinforced CMC has also been studied.

Polysilahydrocarbons belong to a new class of silicon containing polymers in which the polymer backbone consists of Si-(C)x-Si units, where x is more than one. In recent years, a great deal of work has been carried out in the area of polysilahydrocarbons focusing mainly on the synthesis, microstructure and mechanism of formation and thermal stability. However, the thermal degradation kinetics of such polymers and their end-uses have not been studied.
Thus, in addition to the investigation on borosiloxane oligomers, the present thesis focuses on the thermal degradation behavior of polysilahydrocarbons and their evaluation as atomic oxygen (AO) resistant coating for low earth orbit space structures.

The thermal degradation kinetics of polysilahydrocarbons obtained through the dechlorination of diorganodichlorosilanes with styrene has been carried out using four different equations. Attempts have been made to correlate the activation energy and pre-exponential factor with the structure of the copolymers. Similar investigation has been carried out on the polycarbosilanes obtained by heat treatment of polysilahydrocarbons at different temperatures. Attempts have been made to correlate the thermal behavior of polycarbosilanes with the structural changes that take place in polysilahydrocarbons during heat treatment.

The atomic oxygen formed by the photodissociation of molecular oxygen in the upper atmosphere. AO can react with most of the spacecraft materials causing surface erosion which eventually brings down the performance of these materials drastically. Thus, it becomes essential to develop spacecraft materials which are resistant to AO attack or apply AO resistant coatings on the spacecraft materials which are susceptible to AO attack. When inorganic polymers or organometallic polymers are used as protective coatings, they form a metal oxide layer on the surface due to the interaction of the oxidation of the polymer by AO. This oxide layer prevents further interaction of the polymer with AO, thus offering protection to the substrate which is otherwise susceptible to AO attack. As polysila-hydrocarbons contain disilyl linkages, these linkages can trap oxygen forming siloxane linkages which on further reaction with AO would result in the formation of SiO₂ layer. Keeping in view of the above advantage, in the present work polysilahydrocarbons have been evaluated as AO resistant coatings. The performance of these polymers has been compared with other AO resistant materials developed in the Preceramic Polymers Laboratory of VSSC and also with phosphazene-containing polymers.
References


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