Carbosilanes: Reactions & Mechanisms of SMP-10 Pre-Ceramic Polymers

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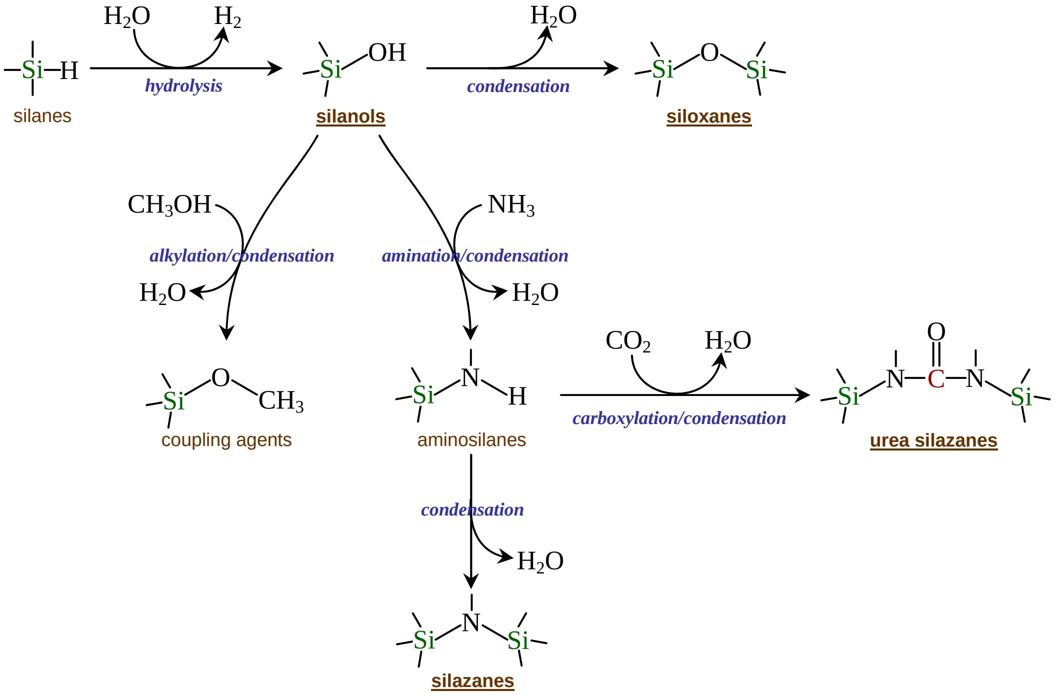
INTRODUCTION TO POLYMERIC CERAMIC PRECURSORS

The field of pre-ceramic polymer science is relatively new (less than a couple of decades) and there is simply not much available in the literature regarding the chemistry and physics of these materials, apart from the vendors themselves, who tend to keep most of the technical aspects proprietary. These proprietary inclinations are especially true in areas pertaining to the specific synthesis pathways utilized, the particular molecular configurations incorporated into their products, and certain aspects of the process chemistry. This lack of information can sometimes lead to problems in comprehending the behavior and full ramifications of the material during end user processing operations and aggressive field exposures. The term 'pre-ceramic' polymer (resin) pertains to specialized polymer/oligomeric materials which contain both organic and inorganic molecular segments and thermally transform into (inorganic) ceramics when 'fired' or subjected to high temperature treatments (pyrolysis). The particular inorganics of interest here are silicon and nitrogen, whose interactions with organic carbon can lead to some unique properties.

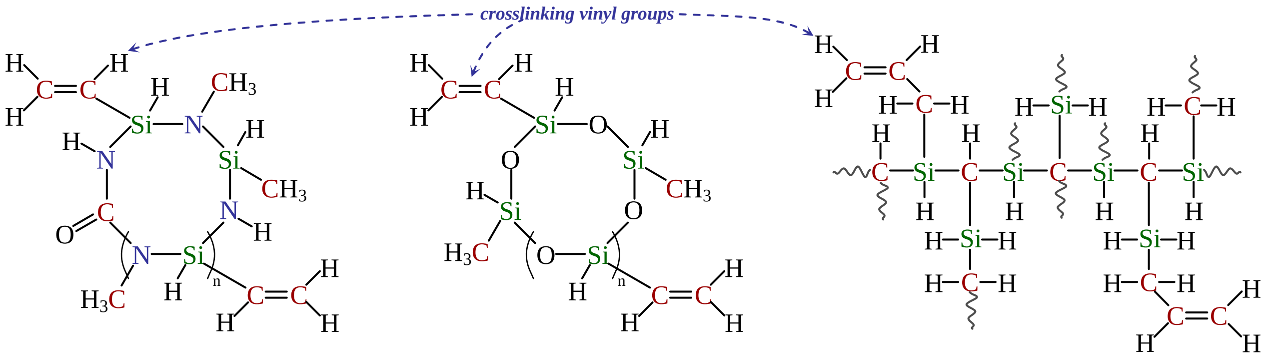
Independent work in this field has provided hands-on experiences coupled with extensive chemical, physical and process characterization of a number of pre-ceramic materials utilized in the areas of CMC composite fabrication & densification, ceramic bonding & joining processes, and ceramic coating techniques. The top three primary families of pre-ceramic polymers include (1) the –Si–C– based carbosilanes (ex. Starfire's SMP-10, formerly marketed as AHPCS polymer), (2) the –Si–C–N– based carbosilazanes (ex. KiON's Ceraset, originally developed and marketed by Dupont's Lanxide division), and (3) the –O–Si–O– based carbosiloxanes or silicon oxycarbides (ex. Honeywell's Blackglas, originally developed and marketed by Allied Signal). In addition, analogues to most of these materials are produced in other countries outside the USA (for example, Nippon Carbon Company of Japan markets its own line of pre-ceramic polycarbosilane products in competition with the Starfire Systems).

The following discussion draws heavily on some of these background experiences. No references are cited since all reaction scenarios, descriptions, illustrations, molecular structures and proposed mechanisms are provided strictly from the author's perspective as derived from experimental studies in formulation chemistry as well as the processing and characterization of a variety of polymeric materials, including the principal ceramic precursors. Additionally, no mathematics is used here as this is an *illustrative* survey of the organic/inorganic chemistry associated with the synthesis and processing of these materials in the author's own personal style of chemical communication and notation. It is not the intent to present advanced nomenclatures or hard-to-understand chemical graphics but to provide a fun and enlightening story about these materials and the chemistry associated with them. As such, no guarantee is made regarding the accuracy or correctness of any of the concepts covered here, however, all comments, questions and corrections are welcome and greatly appreciated.

While carbon and silicon are positioned in the same periodic group and exhibit the same valence state, the reactions and properties of the two are not identical. This is notably apparent considering the reduced ability of silicon atoms to undergo the *sp*^{2} atomic hybridization required for the formation of sigma-pi double bonds or to freely participate in a number of classical reactions characteristic to organic carbon. However, some of the more common functional groups can be attached directly to the silicon atom through sigma *sp*^{3} orbitals. Of particular interest are groups such as chloride –Cl, hydroxyl –OH and amino –NH_2 which comprise the basis for the formation of silanols (similar to organic alcohols), siloxanes (similar to ethers and esters), silazanes and urea silazanes (analogous to amines and urethanes). In most compounds, the central silicon-based functional groups are easily recognized as shown in the diagram below which illustrates a few of the potential synthetic pathways and representative functional group structures for the silanes, silanols, siloxanes, silazanes and ureasilazanes . . .



In general, freshly synthesized versions of most of these polymers (or oligomers), as well as their semi-organic, *carbide*-modified versions (ex. Ceraset silazane and Blackglas siloxane) tend to form ring-like structures during the synthesis process. A couple of examples might include the following structural representations (branched carbosilanes are slightly different and will be covered in the next section) . . .



Urea Silazane Oligomer Unit

Silicon Oxycarbide (Siloxane) Oligomer Unit

Branched Carbosilane Polymer Segment

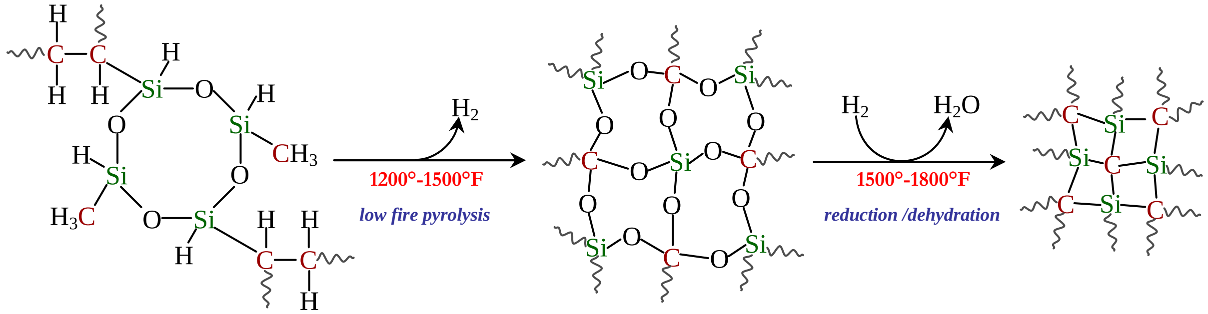
Incorporation of a small amount of peroxide compound into any of these resin mixtures initiates the curing process by providing a source of free radicals which causes neighboring vinyl (unsaturated) groups to crosslink. When heat is also applied, the polymer rapidly undergoes a curing/crosslinking process that converts the liquid resin into a hardened thermoset structure (this is not pyrolysis but is an intermediate curing/crosslinking stage analogous to organic polymer thermosets). These thermoset molecular configurations retain their amorphous structural character as they become comprised of silazane or siloxane units joined together by saturation of the pendant (organic) vinyl groups via free radical addition (crosslinking) between adjacent branches.

Upon low temperature pyrolysis, each of these polymers converts into the respective glassy ceramic at impressively high yields . . . 75-85%. When atmospheric oxygen is allowed to diffuse and incorporate into the structure, ceramic yields can be as high as 95% since oxycarbides and/or oxynitrides comprise a substantial portion of the ceramicized structure. High yields are understandable considering the fact that hydrogen is overwhelmingly the primary gas evolved during pyrolysis (emission of silicon, carbon and nitrogen groups can be kept to a minimum by using the proper controls during the thermal conversion process). Generally, volumetric losses associated with these materials during low fire pyrolysis are moderate (10-15%). However, for long term high temperature exposures, these glassy ceramics must inevitably transform into crystalline forms, either intentionally during processing or during their service lives, which may or may not be desirable.

In some cases, as with the LAS C-C/SiC components, the extent and specific locality of glassy-to-crystalline conversion is purposely controlled and designed into the composite fabrication strategy while it is also allowed to occur later on during the actual motor firing cycle. In this case, the outer surfaces of the articles temporarily receive the benefits of an amorphous ceramic in a motor valve environment which only needs to fire once for a few seconds. In any event, this conversion process typically results in about a 30-40% volumetric loss of the material accompanied by the formation of many voids, cavities, tunnels and general porosity throughout the converted structure. While the expulsion of residual hydrogen may be minimal during the glass-to-crystalline conversion process, the structural and volumetric changes associated with this transformation are quite substantial.

Pyrolysis of silazanes in 100% argon atmosphere yields silicon-based ceramic products which are a mixture of the carbide and the nitride . . . SiC/Si_3N_4. However, when the gas mixture includes increasing levels of reactive ('spoiler') gases, such as hydrogen or nitrogen, the product can be tailored to favor SiC or Si_3N_4. High fire pyrolysis (> ~2500°F) in 100% H_2 gas yields 100% β-SiC, while the same pyrolysis cycle carried out in 100% N_2 or heavy NH_3 would yield 100% Si_3N_4. These results and effects have been personally verified experimentally during extensive studies with these materials.

Preceramic siloxanes, $HO[–SiR_2O–]_nH$, are typically prepared through a sol-gel process. Pyrolysis of these cured materials in 100% Ar gas yields a classic silicon oxycarbide product (SiO_xC_y) which many analytical tools often perceive as SiC-SiO_2 structural mixtures. Incorporation of 'free' carbon into the microstructure 'blackens' the product (ie... Blackglas). Pyrolysis in heavy H_2 atmospheres will ultimately produce SiC, however, this negates the intention of using siloxanes in the first place (more viable precursors are readily available for direct formation of SiC). Similarly, when inertly produced silicon oxycarbide products are subsequently subjected to high temperature treatments or excursions (> ~2400°-2500°F), the SiC-SiO_2 glass structure begins to reduce down to β-SiC with substantial reductions in volume (this is indicative of the temperature limitation for these materials). Post-fire treatment temperatures can be substantially lowered when H_2 gas is utilized as a reducing/dehydration agent (oxygen scavenger) in the post-fire atmosphere. This is illustrated below for the conversion of cured silioxane resin into silicon oxycarbide (glassy) ceramic and then to a-SiC glassy ceramic . . .

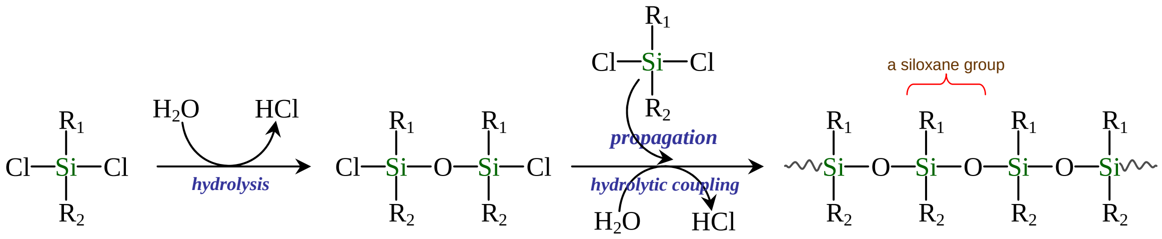


Crosslinked Siloxane Resin **Glassy Silicon Oxycarbide Ceramic** **Glassy a-SiC Ceramic**

Treatment to > 2000°-2200° would crystallize the a-SiC into β-SiC with further (drastic) reductions in overall volume (30-40% as indicated above) along with the accompanying porosity development. Thus, in reducing atmospheres (such as certain solid fuel nozzle environments), the oxycarbides may be expected to experience significant volume shrinkage and porosity creation, but in oxidizing environments (such as the skins and leading edges of lower orbit vehicles), these materials will tend to exhibit a certain degree of relative inertness with much more stability. Oxycarbides would likely demonstrate undesirable effects in reducing NH_3 ammonia environments as well. Effective incorporation of boron into the SiO_xC_y structure has been demonstrated to increase the oxidation protection of these materials.

Generally speaking, treatment of most of the pre-ceramic polymers to temperature levels less than ~2000°-2200°F produce the 'glass' version of the ceramic . . . for example, a-SiC, a-Si_3N_4 and SiO_xC_y are all glass-type amorphous materials generated during low temperature pyrolysis operations. Oxygen-stable Blackglas is exclusively a glassy ceramic until higher temperature treatments convert the amorphous structure into cubic β-SiC. Conversely, most silazane and ureasilazane liquid resins are sensitive to atmospheric oxygen and moisture, as oxygen tends to become incorporated into the ceramic structure producing oxycarbide segments in accordance with the level of oxygen absorbed. During the molecular design stage of these products, the more that silicon-bound hydrogen atoms can be substituted with other groups, the less sensitive the polymers are to oxidation/hydrolysis. Active hydrogen atoms attached directly to silicon atoms represent the primary hazard associated with these types of materials as flammable hydrogen is continuously expelled during storage and throughout user-applied processing.

In the field of *silicones*, carbon entities are incorporated into the molecule as pendant *side groups* attached directly to silicon atoms along the –Si-O-Si– backbone. Thus, these materials are also semi-organic, containing silicon, carbon, oxygen, hydrogen and sometimes other elements. While chlorinated silane monomers have generally been replaced with safer alkoxy versions, a classical synthetic route to the silicones involves the reaction of a dichlorosilane with water to give an alkyl polysiloxane . . .



a dichloro silane

Step-Wise Synthesis of Silicone from Dichlorosilane

an alkyl substituted polysiloxane (non-crosslinked silicone)

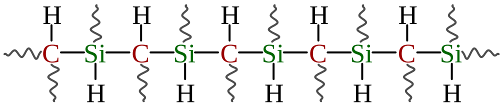
The polymerization reaction proceeds via S_N1 substitution and the organo chlorinated silane monomer is formed by Grignard synthesis (both S_N1 kinetics and Grignard coupling are further defined shortly). Incorporation of lesser amounts of trichloro- and tetrachloro- silane into the reaction mixture allows the synthetic formulator to control the level of branching in the final product. Here, the R_1 and R_2 groups are generally organic (aliphatic, aromatic or both) and are selected based (partially) on the particular mechanism of crosslinking desired for the end product (ex. sealants vs. coatings). For instance, unsaturated groups allow for free radical crosslinking while alcoholic-laden side groups lead to condensation-type crosslinking processes, either of which are generally initiated by the end-user. The quantity of available crosslinking groups determines the degree of hardness, solvent resistance and *elasticity* in the final (cured) product. The absence of crosslinking groups allow these organosilanes to retain their special thermoplastic/elastic properties (a unique form of elasticity is imparted in the silicones due to the nature of bending flexibility between Si and O atoms). In general, pendant groups high in aromaticity tend to increase hardness and temperature resistance of the overall material (the more benzene rings there are in the side groups, the tougher and stiffer the final polymer is). High aliphatic content does just the opposite by imparting 'soft' characteristics to the crosslinked network (along with lower temperature resistance). Pendant groups can also contain functional agents designed to influence lubricity, coupling, wetting, dispersion, blocking, catalysis, and hydrophile/hydrophobe solvency.

In any case, the primary polymer backbone comprising the family of products classified as 'silicones' is –Si–O– siloxane based . . . even though the these polymers contain high levels of both silicon *and* carbon as the primary constituents, they do not typically exhibit the same properties as the silazanes or carbosilanes. All of these product families can be considered as semi-organic and classified as organosilanes. The properties of the silazanes, ureasilazanes and carbosilanes are similar in many respects, particularly in terms of their response to pyrolytic conversion and pre-ceramic properties, while the silicones are slightly different. By functionality, silicones are technically classified as siloxanes and bear more commonality to the silicon oxycarbides. Using the appropriate molecular configurations and processing conditions, silicones comprise their own family of Si-based ceramic precursors, thermally transforming into glassy SiO_xC_y (and eventually a-SiC and β-SiC as illustrated above).

Indeed, in the 1990's, Dow Corning marketed their own line of silicone-based pre-ceramic materials, including resins and SiC fibers, but then later sold off this portion of their CMC business. They appear to still be involved in markets serving the silicon oxycarbide industries which utilize SiO_xC_y-type resins, coatings and composite matrices (Blackglas, developed by and once a long time product offering of Allied Signal is now owned by Honeywell). While the silicones may be good precursors for oxygen-based ceramics, extreme process modifications are required to achieve respectable SiC yields.

SYNTHESIS OF SMP-10 ALLYL HYDRIDO POLYCARBOSILANE RESIN

Carbosilanes comprise the family of semi-organic polymer resins characterized by a molecular configuration in which carbon and silicon atoms are covalently bonded directly to one another in an alternating fashion along the primary polymer chain segments . . .



Note: 〰 simply means a continuation of the structure not shown

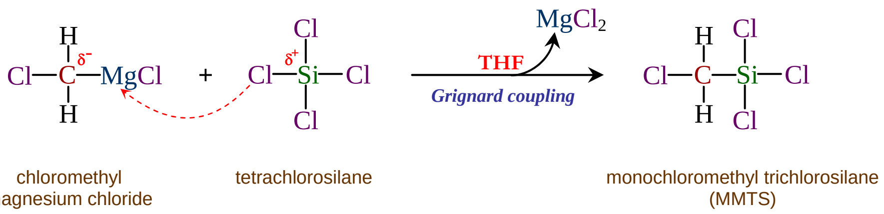
alternating sequence of carbon-silicon atoms along a linear segment or chain in a carbosilane polymer/oligomer

Additionally, these methylene-linked silicon structures are typically comprised of linear segments which are highly branched, with little cyclization. Obviously, the regional ‘closeness’ of carbon and silicon atoms along the virgin chain facilitates the formation of near-stoichiometric SiC in the final pyrolyzed product (indeed, the two atoms are already bonded together in semi-organic form). However, formation of any kind of polymer which can readily transform into stoichiometric SiC upon firing is no small accomplishment. The particular synthesis approach developed by Starfire Systems to make SMP-10 is unknown or ambiguous at best. Long time personal associations with the principal founder and developer of Starfire SMP-10 polymer has permitted opportunities to keep abreast of certain technological aspects and to track the history of this unique material as it has undergone improvements and refinements over the years. It is known that Starfire scientists worked several years to develop a synthesis method that was consistent and fruitful, and they had to overcome many problems before finally refining the techniques that led to their first marketed product, allyl hydrido polycarbosilane, or AHPCS for short.

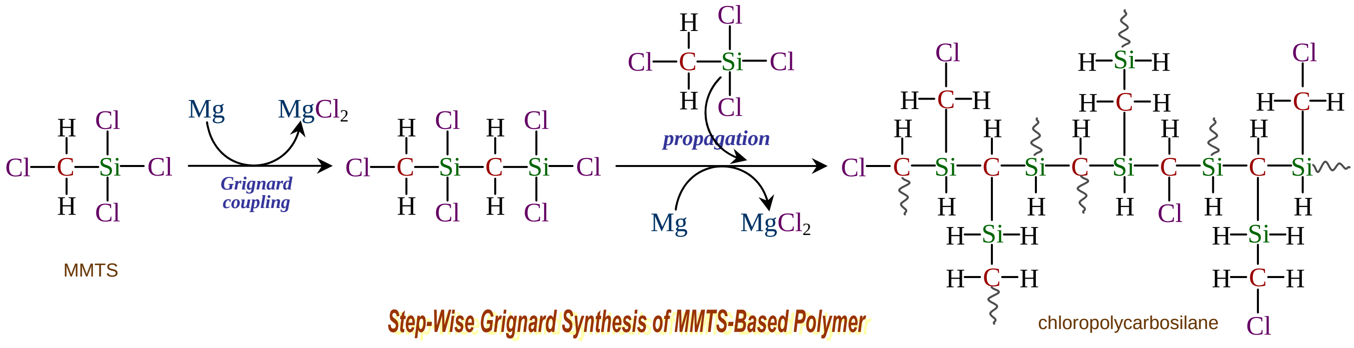
The particular carbosilanes of interest here involve two stages of resin synthesis . . . formation of the hyperbranched carbosilane oligomer backbone and then the attachment of unsaturated pendant side groups. These unsaturated side groups allow the end user to cure (harden) the material prior to pyrolytic ceramicization by inducing crosslinking reactions between neighboring polymer branches. This two stage approach is not uncommon in the various fields of organic thermosets (ex. acrylic or styrene monomer crosslinked polyester resins are widely used as commercial fiberglass resins and coating lacquers). It is also known that Starfire workers experienced great challenges during development activities associated with the second stage of the synthesis process. Much effort was expended in attempts to attach common vinyl groups to open branches within the carbosilane polymer network which would facilitate subsequent crosslinking in an effective and consistent manner. Eventually, proper incorporation of *allyl* groups led to the successful product sold as AHPCS polymer (note that allyl = propenyl = methyl vinyl).

Minor refinements in the polymer structure along with more fashionable trade name nomenclature for their growing line of AHPCS-based products eventually led to the now famous SMP-10 polymer which is, at the very least, the basic ingredient for the company’s primary line of product offerings (in order to avoid confusion, it should be realized that SMP-10 *is* AHPCS). Products offered by Starfire based on SMP-10 polymer range from ultra-low viscosity CVD polymers to liquid fiber coating dips to composite matrix resins and slurries. Understandably, the specific techniques and reaction pathways employed to synthesize AHPCS/SMP-10 polymer have generally been proprietary. However, techniques for attaching carbon atoms directly to silicon can be surmised given the vast resource of potential reaction scenarios defined in the field of organic chemistry. Of particular interest here are the reaction approaches involving Grignard reagents and *Grignard synthesis*. Grignard agents are haloorganometallic compounds (or molecular segments) which induce coupling with another molecule, end-segment or agent containing halogen. For most applications, the Grignard functional group consists of magnesium chloride, R_1–MgCl, while chloride is also the halogen attached to the co-reactant R_2–Cl. These –MgCl agents are very reactive, as they will react readily with H_2O, CO_2, O_2, NH_3 and many other organic/inorganic functional groups. Grignard reactions must be conducted under completely anhydrous conditions.

Grignard agents are unique to organic carbon since the carbon atom attracts electrons from the electropositive magnesium atom forming a covalent bond between the two, while the magnesium and chloride atoms ionically bond together. This organometallic complex exhibits high polarity. Other metals (such as copper and lithium) as well as the other halogens (Br and I) can also form Grignard reagents, depending on the desired effects. Of special interest here is the reaction between the family of magnesium chloromethanes and those of the chlorosilanes as a starting point for carbosilane synthesis as depicted below. Here, a silyl chloride attacks the MgCl group causing silicon to become slightly positive while carbon becomes negative (a carbanion). As the two entities combine, $MgCl_2$ is ejected . . .



The product of this reaction, monochloromethyl trichlorosilane (MMTS) is considered to be the primary reactive monomer ultimately leading the formation of polycarbosilane. It can be surmised that the di- and tri- chlorinated versions of both the methyl and silyl reactants are also synthesized and strategically incorporated into the reaction mixture at controlled levels to influence the nature, frequency, content and length of branching throughout the growing molecule. For the intended purposes here, MMTS can be used to illustrate the typical reaction pathway leading to the highly branched, chlorinated carbosilane first stage polymer via Grignard synthesis . . .

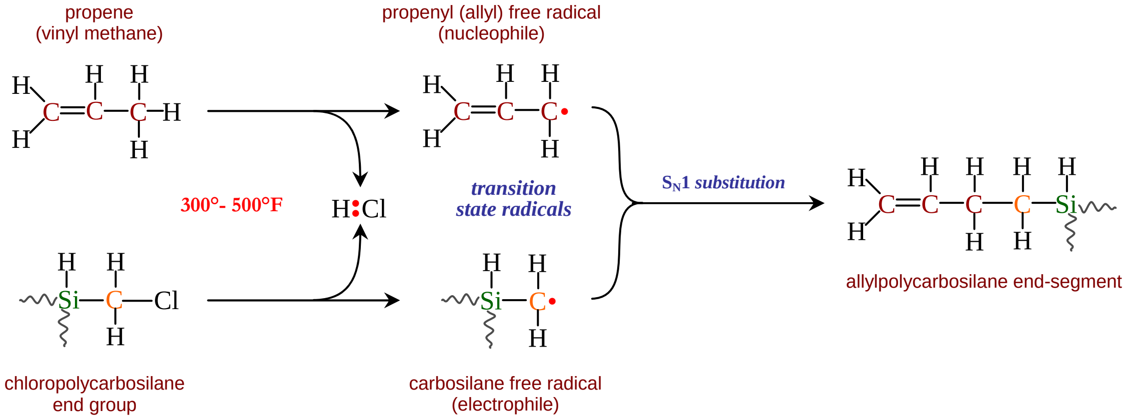


Step-Wise Grignard Synthesis of MMTS-Based Polymer

As can be seen, this intermediate product is laden with residual chlorine in which –Cl groups are retained at most of the unreacted sites. Ultimately, all these chloride groups must be extracted from the system and this can be accomplished by treatment of the chlorinated polymer with the appropriate reducing agent. However, before reduction operations are implemented, it should be recognized that these –Cl groups are key to providing an attractive and compatible method for incorporation of the allyl crosslinking groups into the macromolecule.

Independent resources have indicated that the allyl content in as-received AHPCS/SMP-10 polymer runs around 10 to 15%. During the second stage of the synthesis process (attachment of the allyl groups), it can be surmised that some of the objectives are to . . . (a) incorporate a few of these groups along the outer fringes of the polymer clusters, (b) avoid excessive allylation of the polymer adduct, (c) ensure uniform distributions of allyl groups throughout the branches of each macromolecular cluster, and (d) prevent allyl groups from penetrating deep into the polymer core where their reactive effects may be sterically hindered later on. It should be noted that each incorporated allyl group changes the Si:C stoichiometric balance of the ceramic precursor, and every group that is added in excess of the molecular design strategy will inevitably lead to a 'carbon rich' ceramic product. Undoubtedly, it was essential for Starfire scientists to develop a rather innovative technique to effectively distribute the optimum level of allyl (propenyl) groups at the desired positions along the polymer periphery.

There are at least two possible pathways capable of facilitating the attachment of allyl pendant groups onto the intermediate polymer end-branches. One approach involves a mechanism of free radical substitution directly utilizing propene to incorporate the allyl groups. As propene gas is bubbled through the chlorinated polymer mixture at elevated temperatures, HCl gas is generated when allylic carbon displaces chlorine in the mother structure. A possible scenario for the attachment of allylic (propenyl) groups onto end-braches in the chlorinated polymer via free radical substitution might be . . .

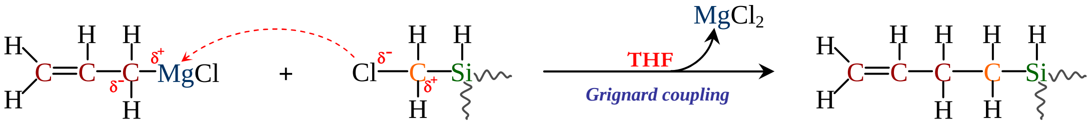


Here, propene and the chlorocarbon end-group dissociate into their respective free radicals where the nucleophillic propenyl radical couples with available (unhindered) electrophillic carbosilane radical end-groups. Chloride functions as the 'leaving group' and the reaction mechanism is expected to favor S_N1 kinetics over S_N2 because . . . (a) steric hindrance is significant due to the structural shielding effect imparted by the highly branched polymer (poor access to reaction sites discourages backside attack and chiral inversion which are characteristic of S_N2 substitution), (b) chloride is a relatively strong base (weak basic leaving groups favor S_N2 substitution), and (c) the reaction is likely carried out in an aprotic solvent such as tetrahydrofuran (THF) or dialkyl ether (protic solvents such as water and alcohols are characterized by hydrogen bonding which tend to favor S_N2 kinetics).

Note 1: An allylic carbon atom is one that is adjacent to a double bond . . . it is the alpha carbon directly attached to the vinylic carbon which forms half of the double bond in a vinyl group. Propene (or vinyl methane) is the simplest allylic compound. Due to resonance, allyl compounds readily form very stable radicals (low bond dissociation energy) which accounts for their high reactivity towards substitution. However, ionic addition to the double bond is a competing reaction which must be minimized by careful control of the reaction conditions. As the nucleophillic propenyl radical is formed, bonding between all three carbon atoms is converted from sp^3 hybridized σ orbitals to sp^2 $\sigma-\pi$ combined orbitals (a nucleophile is a negative reactant seeking a cation). In general, the symmetric allyl radical is a hybrid of two equivalent resonance structures where the π bond and the unpaired electron are delocalized across the entire molecule allowing substitution to occur at either end-carbon.

Note 2: The acronym S_N1 refers to substitution-type reaction mechanisms which follow first order (unimolecular) kinetics and which involve one but sometimes both nucleophillic and electrophillic reactants to varying degrees. The primary reactant of interest in most of these cases is the negatively charged nucleophile (which seeks a nucleus) and determines the overall rate of the reaction. So the term S_N1 stands for unimolecular nucleophillic substitution. In contrast, substitution reactions which involve less structurally complex (branched) reactants (where steric factors are less significant) and weaker basic leaving groups often tend to involve both reactants significantly (opposite to nucleophiles, electrophiles are attracted to negative entities rich in electrons). This leads to second order reaction kinetics whose rate is dependent equally on the concentration of both reactants. Such cases are designated by S_N2 which stands for bimolecular nucleophillic substitution.

The other possible scenario for attaching allyl groups to polymer end-branches within the reaction mixture calls for utilizing the *allyl Grignard reagent*. Again, during the transition state, magnesium Mg^{+2} is attacked by chloride Cl^- causing the end carbon on the polymer to become an electrophillic carbocation which reacts with the nucleophillic alpha carbon in the allyl Grignard agent (the alpha carbon becomes a carbanion), and as the two reactants join together, magnesium chloride is expelled as a by-product . . .



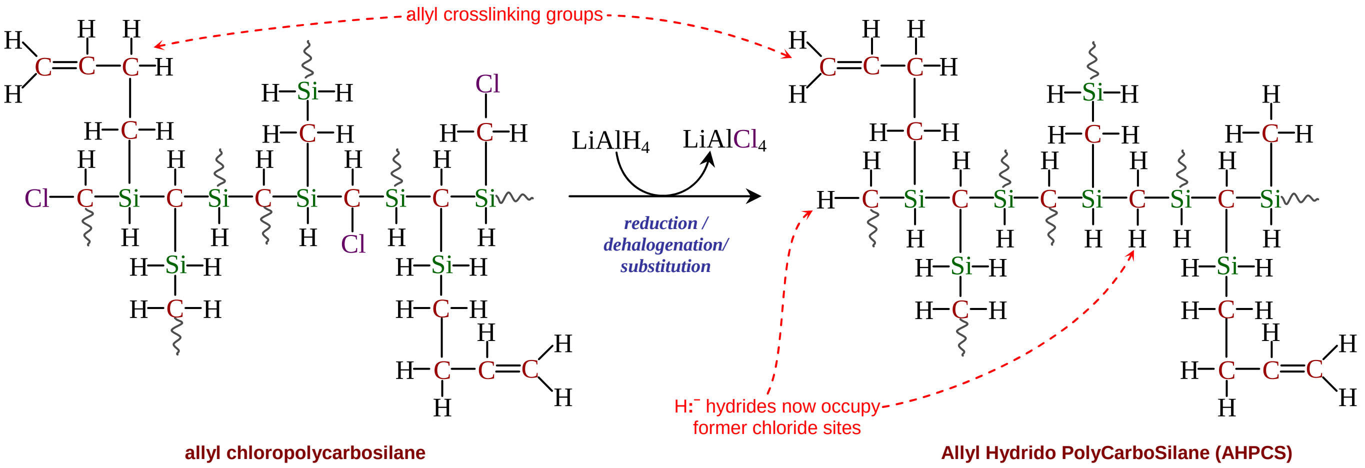
propenyl (allyl)
magnesium chloride

chloropolycarbosilane
end group

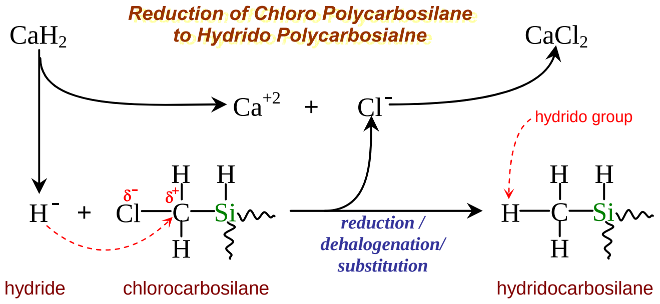
allylpolycarbosilane end-segment

After incorporation of the crosslinking groups has been successfully completed (the goal is probably about 15-20% allylic substitution), there will be a substantial quantity of residual chloride groups remaining throughout the polymer network which must be eliminated or extracted from the system. Since chloride is a moderate reducing agent, a likely approach for its removal (dehalogenation) is substitution with a stronger hydride-type reducing agent. The most prominent and readily available reducing agent for these types of scenarios is lithium aluminum hydride, $LiAlH_4$.

Alternatively, the reducing agent calcium hydride, CaH_2 may also be feasible for this application. $LiAlH_4$ is more soluble in THF as a reaction medium than the commonly used diethyl ether solvent, while the solubility of CaH_2 in any solvent is quite limited. Both agents are extremely sensitive to atmospheric moisture and must be used under highly controlled reaction and storage conditions. Unfortunately, both can react violently with chlorocarbon compounds under certain conditions, so Starfire workers must have overcame some steep challenges during development of this step. A likely reaction scenario for dehalogenation of the chlorinated polymer via reduction with $LiAlH_4$ is illustrated below . . .



Replacement of the chloride groups with hydrogen atoms, or more specifically, *hydride* $H{:}^-$ groups, leads to the AHPCS/SMP-10 polymer structure with inclusion of the 'hydrido' nomenclature to the naming system. A hydride group is a negatively charged hydrogen ion, and a very strong reducing agent, which carries two 1*s* electrons, as opposed to a neutral hydrogen atom (radical) containing only one electron, or the more common hydrogen cation H^+ well known for its acidic properties (a solvated proton). Now, reduction/dehalogenation with CaH_2 would proceed according to the same mechanism as that associated with the use of $LiAlH_4$ . . .



Here, the nucleophillic hydride ion is formed opposite to the more electropositive calcium ion Ca^{+2} (or $LiAl^{+4}$ in the case of $LiAlH_4$) and behaves almost like a halogen or a hydroxyl group displacing chloride from the polymer perhaps following kinetics similar to S_N1. In either case, residual inorganic impurities left behind from the synthesis process, primarily the reduction step (traces of Li, Al and/or Ca), must be cleaned from the system and this is probably done by careful extraction or washing with water. While the respective ions of Li, Al and Ca are readily soluble in water, both of these reducing agents will also undergo hydrolysis, producing effervescing hydrogen gas while the corresponding insoluble hydroxide falls out of solution and is filtered out . . .

$$CaH_2 \quad + \quad 2\,H_2O \xrightarrow{\textit{hydrolysis}} Ca(OH)_2\downarrow \quad + \quad 2\,H_2\uparrow$$

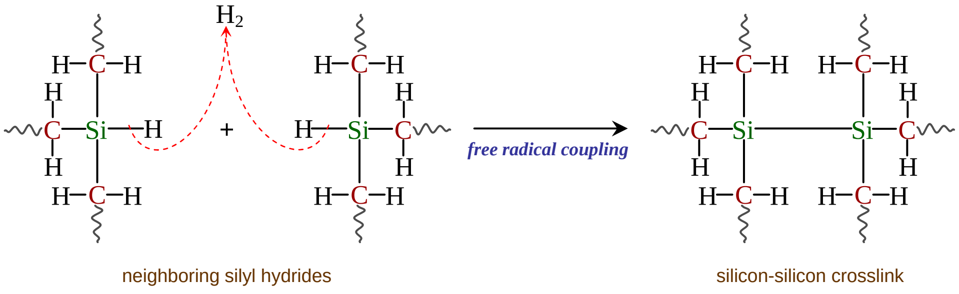
Lastly, a series of drying steps must be applied to the virgin polymer in efforts to remove all traces of water and moisture from the system. A likely drying agent for this purpose is calcium chloride $CaCl_2$. It is well known that these polymers are sensitive to water, which can be absorbed during handling, storage and end-user procedures. Thus, extra caution must be practiced to minimize hydrolytic degradation of the material during the synthesis stages all the way through the final user-application processes.

USER APPLIED CROSSLINK PROCESSING AND PYROLYSIS OF SMP-10

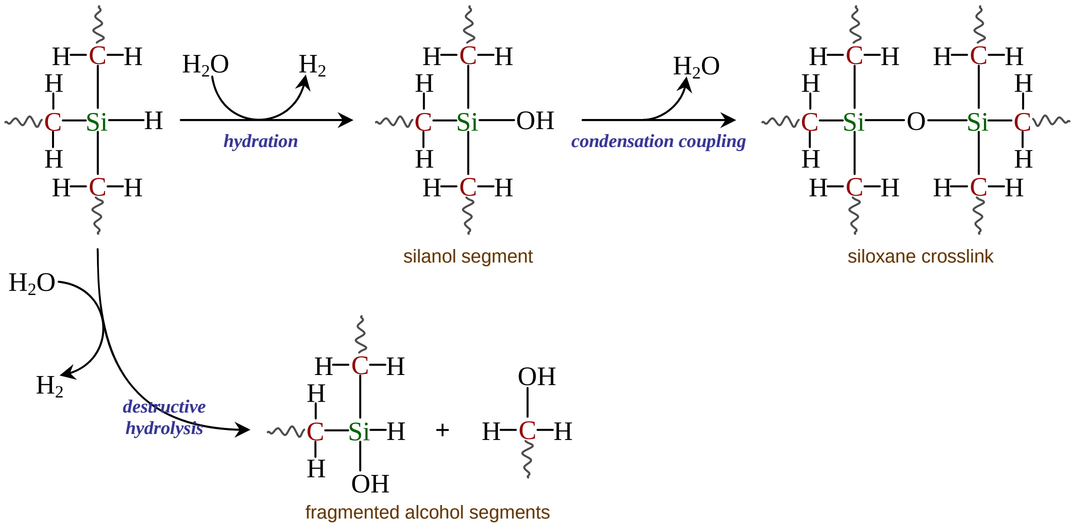
Before the AHPCS/SMP-10 resin is cured (throughout it's life in the liquid state), the polymer evolves hydrogen gas and remains reaction-sensitive to atmospheric moisture until it is hardened by cure. The cured product continues to emit hydrogen all the way through pyrolysis until it is finally converted into ceramic form. These properties also apply to the silazanes and ureasilazanes covered earlier. In addition, the pre-ceramic resins are very sensitive to acids, bases and catalytic metals, sometimes rapidly expelling H_2 and forming flammable and explosive mixtures in air. Without a doubt, the end-user should develop safe practices and remain cautious during the storage, handling and application of these kinds of resins because hydrogen gassing can result in pressure build-up, fire, and/or explosions.

Hydrogen atoms attached to silicon are not the same as carbon-bound hydrogens. The silicon-to-hydrogen bond is longer and weaker than the carbon-to-hydrogen sigma bond. Silicon-bound hydrogen atoms are so available that many silane compounds, particularly silane itself SiH_4, are often used as reducing agents (ordinary silane, often called silyl hydride, is a strong hydride $H{:}^-$ donator). All compounds containing Si–H bonds can generate hydrogen spontaneously. Additionally, they are hygroscopic, readily absorbing and reacting with environmental moisture and oxygen. Thus, the three less-than-desirable reaction effects associated with these types of liquid pre-ceramic polymers *before* they are ever even subjected to user-applied curing and processing involve . . .

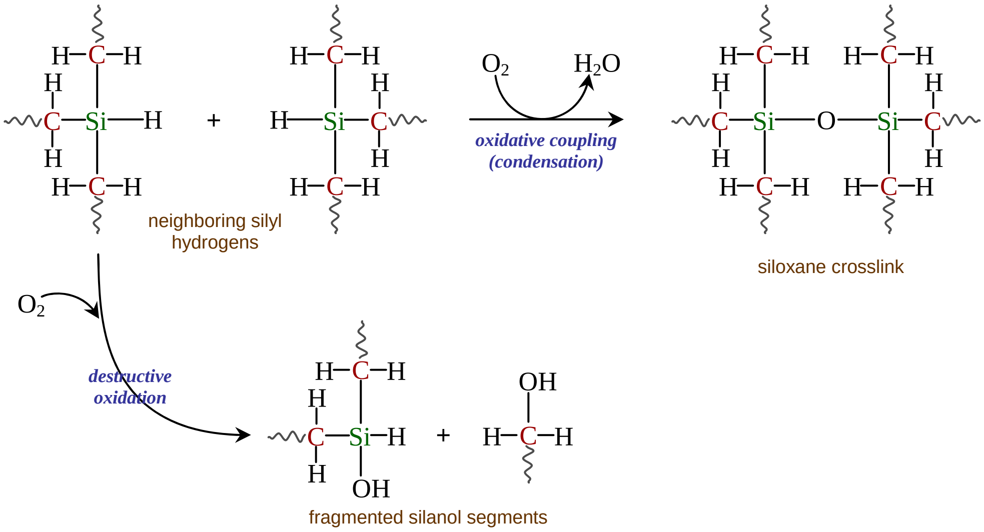
(1) The evolution of hydrogen gas, which is believed to be (partially) due to reactions between neighboring hydrogen-silane segments within the entangled polymer network. Essentially, this is a form of 'crosslinking' between local silyl radicals, and involves the bridging of two silicon atoms . . .



(2) Hydration/hydrolysis of silyl hydride groups along the polymer chain with the formation of silanol groups. Latent residual water within the polymer system and absorption of environmental moisture are the culprits to this effect. The reaction creates hydrogen gas (yet another source of hydrogen generation) and may proceed along two paths with very different results . . . one facilitating the formation of siloxane linkages between neighboring silanol groups via condensation and the other leading to destructive scission and fragmentation of the polymer chain into alcoholic end-segments . . .



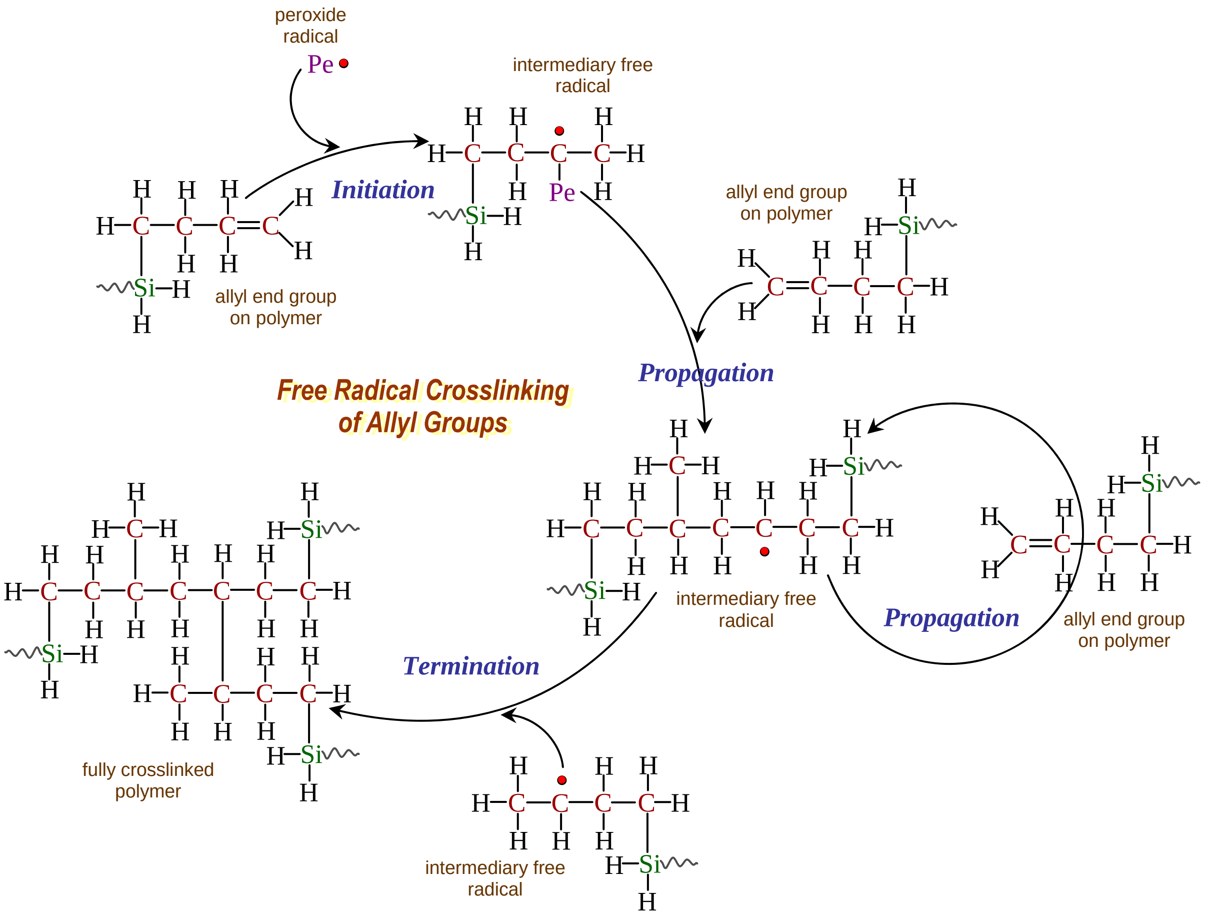
(3) Oxidation of silyl hydride groups along neighboring polymer chains. In a similar fashion as reaction (2), oxidation can proceed along two tremendously different paths . . . siloxane coupling (crosslinking) via condensation or destructively, with the formation of fragmented silanol segments . . .



Other than the evolution of dangerous hydrogen, the coupling reactions are not necessarily degradative to the polymer network, but they could conceivably have anomalous effects on the optimal performance of the pre-ceramic material (either path represents aging and unintentional variation within the resin). However, the more damaging effects of chain scission leading to fragmentation of the polymer structure are often catastrophic, though under extremely favorable conditions, these cleavage reactions may be partially reversible, possibly re-coupling the fragments through condensation. Similar analogies to all these processes could easily be defined and illustrated for the silazanes and ureasilazanes. Properly synthesized siloxanes (silicon oxycarbides) are significantly more stable toward these types of degradative processes and often become the ceramic precursor of choice for lower temperature applications (< ~2500°F), particularly those requiring higher levels of oxidation protection.

Now . . . the intended reactions and processes for SMP-10, as well as all the other pre-ceramic materials, include (a) curing/crosslinking to harden the thermoset polymer and then (b) pyrolysis to convert the hardened polymer into ceramic (SiC in the case of SMP-10). If the freshly synthesized liquid polymer adduct is subjected to high enough temperatures (~300°-400°F), some of the allyl groups will eventually break down into free radicals. Once of few radicals are formed, crosslinking of the polymer (through the attached allyl groups) takes off spontaneously via chain reaction (in shop lingo, the resin 'kicks off'). Alternately, if a small amount of peroxide (1-3%) is mixed into the resin, the peroxide will break down into free radicals at a much lower temperature, kicking off the crosslinking process without the need for high temperature exposure. From a safety perspective, the particular organic peroxides used to crosslink these types of polymers should be free of oxygen and protic hydrogens. They can consist of aliphatics, aromatics or any combination thereof . . . butyl and cumyl peroxides are examples.

Thus, crosslinking between local allyl groups in the SMP-10 system occurs throughout the material and proceeds across three graduating stages . . . (1) *Initiation* (generation of the initial free radicals); (2) *Propagation* (addition of radicals to other local allyl groups as the product molecules grow in size and themselves become newly created radicals); and (3) *Termination* (when the last few radicals combine forming non-radicalized products, the reaction process rapidly falls off) . . .

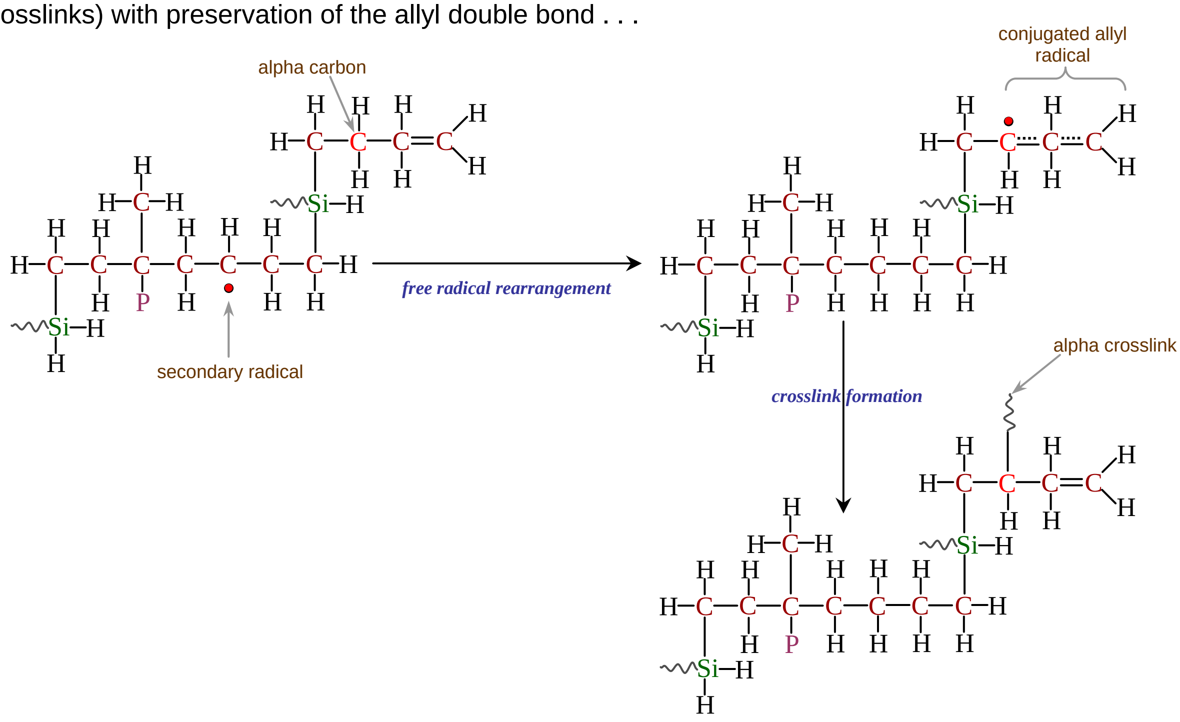


Here, a peroxide radical P• adds to an allyl double bond creating a new, larger radical which itself then adds to another local double bond creating an even larger radical, and so on. It can also be seen from the illustration above that the more allyl groups incorporated into the polymer, the more the Si:C stoichiometric ratio deviates from unity and the more 'carbon rich' the final product will tend to be. Eventually, all the double bonds in the system become saturated (crosslinked) and the chain reaction grinds to a halt. Not shown in this scenario however, are the intermediary propagation steps illustrating the tendency for most newly formed radicals to 'rearrange' in order to form more stable radicals in accordance with the laws of energetics. Ordering of organic free radical stabilities generally runs according to . . .

Stability of Free Radical = Ease of Formation =

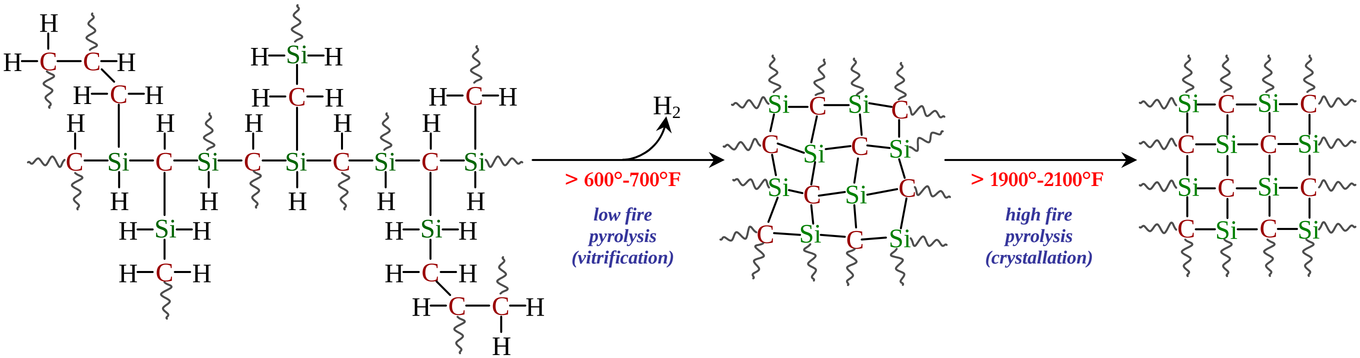
benzyl > allyl > tertiary > secondary > primary > methyl > vinyl

This ordering may shed some light on why Starfire workers were able to incorporate allyl groups into the structure but experienced great difficulty with vinyl groups. To avoid confusion, once the allyl double bond is saturated by a radical, the tricarbon group no longer retains its former allylic identity but becomes a secondary group (recall that resonance-stabilized allyl radicals are generated during the original synthesis process when these groups are incorporated onto the polymer end-segments as the *alpha* carbon carries the radical electron – see page 8). However, depending on the local molecular structure, there will be cases where the radical electron can shift to a nearby tertiary carbon, thus lowering the local energy. Inevitably, a radical electron will also shift to the alpha carbon of a local unsaturated allyl group, which can lead to conjugated-assisted crosslinking at the alpha carbon (alpha crosslinks) with preservation of the allyl double bond . . .



As noted, during this type of crosslinking, the original allyl group remains intact. This double bond can then go ahead and interact with other local segments to form a normal crosslink, as long as steric hindrance permits. In any case, since there is an unrelenting supply of free hydrogen generated throughout the system, a certain fraction of the double bonds will inevitably become saturated with hydrogen as the uncured material ages, which imposes undesirable shelf limits on the resin.

Finally, as the cured polymer is subjected to ever increasing pyrolytic temperatures, it is first converted into an amorphous, glassy form of SiC, designated as a-SiC. This transformation process likely begins around 600°-700° and continues as the temperature is gradually increased, up until about 2000° ± ~200°F. Inert pyrolysis operations kept below this temperature range can be designated as 'low fired' or 'low temperature pyrolysis'. Above the 2000°-2200° range, the a-SiC ceramic begins to crystallize and convert into its face-centered cubic beta form, β-SiC. In this context, inert process temperatures greater than about 2400°-2500°F are understood to mean high fire or high temperature pyrolysis. The structural changes associated with these conversion effects are illustrated below . . .



cured SMP-10 carbosilane polymer

glassy/amorphous a-SiC

crystalline cubic β-SiC

It has been well established that these materials undergo significant volume shrinkage as they are converted into their ceramic forms. As eluded to earlier, the cured polymer will lose about 10-15% of its original volume during conversion into a-SiC and then another 30-40% as the amorphous structure undergoes crystallization. These general ranges also apply to the other pre-ceramics as well. It should be emphasized here that substantial porosity development accompanies these volume changes, particularly when the material converts into the crystalline phase. Thus, applications completely transforming these pre-ceramics into β-SiC, generally require some form of densification-type follow-up procedures to fill up the pores (via CVD/CVI or pre-ceramic polymer impregnation). Undoubtedly, for high temperature applications (>~2500°F), the optimal performance of the pre-ceramics are acquired only after multiple densification treatments (cycles) in which the polymer is applied, cured and pyrolyzed.

The low fired glassy forms of the carbosilanes and ureasilazanes are expected to contain an interconnected micro-porosity network created by the expulsion of hydrogen gas throughout the curing and pyrolysis stages. Due to the nature of these glassy monoliths as they undergo vitrification, a certain level of closed porosity and hermetically sealed voids also form, which later become opened up and expanded during high fire pyrolysis. Even though some workers in the field practice one step procedures with these resinous materials, single shot treatments for critical applications and articles are simply inadequate for coatings, bonded joints or stable high density substrates, unless the goal is a porous product or exposed substrate. Also, it should also be understood that the properties of glassy a-SiC and cubic β-SiC are substantially different. While the bulk densities of a-SiC and β-SiC have been measured to be about ~2.4 and ~3 g/cc respectively, their CTE's run around ~2.5 and ~4+ ppm. Thus, as it is with the various carbon allotropes, not all SiC forms are created equal. Before crystallation of the 'a' phase takes place, mixtures and interfaces of a-SiC and β-SiC behave as two different materials.

DEGRADATION REACTIONS OF SIC CERAMICS IN USE ENVIRONMENTS

While SiC is inert in almost any environment up to > 3000°-3100°F, under extreme situations, it may begin to break down, degrade, transform into a less stable form and sometimes even volatilize. Firstly, in oxidizing atmospheres above about 2000°, the outer molecular layers of SiC will begin to convert into the corresponding oxide SiO_2 (silica or silicon dioxide). This is analogous to the native or passive oxide that forms naturally on many metal surfaces at ambient conditions but which thermally forms on the surfaces of silicon and its compounds after high temperature exposures. It is responsible for the well known oxidation protection provided by SiC articles at elevated temperatures. Depending on gas mixture compositions and temperature distributions across the surface of a hot SiC article, the oxide layer may be uniform in thickness and expansive across the surface or it may be irregular and spotty. While liquid oxygen-type rocket fuels are obviously high in oxygen content, many solid rocket nozzle plumes become depleted oxidation environments, or reducing atmospheres.

At around 2000°F and under sufficient partial O_2 pressure exposures, surface oxidation is thermodynamically favored, which results in the rapid formation of a thin film of glassy (vitreous) silica. This is a self-forming, self-limiting, sacrificial conversion process involving the outer molecular layers of the SiC substrate article with O_2 gas along the gas-solid interface. Above about 2100°-2300°F, the SiO_2 film thickens and densifies, resulting in slower oxygen diffusion (through the film) and thus, a slower oxidation rate. Above about 3000°F, interfacial reactions between the SiO_2 film and the SiC substrate itself become significant, resulting in the formation of volatile SiO and CO compounds. These gaseous products will tend to rupture the SiO_2 film, opening up new channels for more oxygen to diffuse in . . . and oxidation continues. The melting point of SiO_2 varies from about 2900° to 3100°F depending on the particular polymorph or structural form and the environmental pressure on the surface. Crystalline forms such as quartz and cristobalite possess melting points near the upper range while amorphous (glassy/vitreous) SiO_2 structures will liquefy near the lower end.

In cases where surface oxidation of SiC is taking place, the reaction scenario can be outlined as follows. First, 'passive' oxidation of the outer SiC layer begins around 2000°-2100°F . . .

$$\mathrm{SiC}\,(s) \quad + \quad \mathrm{O_2}\,(g) \xrightarrow{\sim 2000°\text{-}\ 2100°F} \underset{\text{amorphous silica}}{\mathrm{SiO_2}\,(s)} \quad + \quad \underset{\text{amorphous carbon}}{\mathrm{C}\,(s)}$$

Passive Oxidation of SiC

The passive silica formed is a thin, dense (nonporous), vitreous film of SiO_2 which grows inward as it consumes the outer molecular layers of the SiC substrate. At higher temperatures, interface reactions between the oxide and the SiC substrate may occur. Under the right conditions, this could conceivably lead to volatilization of the SiC substrate. The process is more substantial for environments containing supplemental oxidizing agents, such as water (covered shortly). However, under extreme temperatures and oxidation levels, some of the SiC may undergo degradation with volatilization . . .

$$2\,\mathrm{SiO_2} \quad + \quad \mathrm{SiC} \xrightarrow{>\ \sim 3000°F} \underset{\text{volatilization}}{3\,\mathrm{SiO}\uparrow \quad + \quad \mathrm{CO}\uparrow}$$

Degradative Interface Oxidation

In aggressive cases, when the overall rate of oxidation exceeds that of oxide replenishment, oxidation converts from 'passive' to 'active' as exposed SiC surfaces begin to degrade and volatilize . . .

$$\mathrm{SiC}\ (s) \quad + \quad \mathrm{O_2}\ (g) \xrightarrow{>\ \sim 3000^\circ\mathrm{F}} \mathrm{SiO}\uparrow \quad + \quad \mathrm{CO}\uparrow$$

volatilization

Active Oxidation of SiC

In *anhydrous* oxidative conditions, the amorphous silica does not undergo de-vitrification or crystallization, even at high temperatures. However, if an influential level of water is present in the flame or environment, a crystallized silica phase may indeed develop. In many cases, the presence of hot water vapor can cause a thick, porous, non-protective layer of cristobalite (crystalline silica) to develop on top of the thin vitreous silica passivation layer. Apparently, the action of water enhances or accelerates the oxidation process by exerting its own oxidative power leading to hydrolytic degradation of SiC, not only into SiO_2, but also with it's volatilization . . .

$$2\,\mathrm{SiC}\ (s) \quad + \quad 3\,\mathrm{H_2O}\ (g) \xrightarrow{\sim 2000^\circ\text{- }2100^\circ\mathrm{F}} \mathrm{SiO_2}\ (s) \quad + \quad 3\,\mathrm{H_2}\uparrow \quad + \quad \mathrm{CO}\uparrow$$

volatilization

Hydrolytic Oxidation of SiC

For a flame mixture containing both O_2 and H_2O, thermal hydrolytic oxidation of the SiC substrate is the primary degradation mechanism at work, and this combination is more devastating than just oxygen alone.

On the other hand, water can sometimes have the opposite effect on the oxide phase as SiO_2 is reduced to silane and volatilization of the silica phase occurs . . .

$$\mathrm{SiO_2}\ (s) \quad + \quad 2\,\mathrm{H_2O}\ (g) \xrightarrow{\sim 2000^\circ\text{- }2100^\circ\mathrm{F}} \mathrm{SiH_4} \quad + \quad 2\,\mathrm{O_2}\uparrow$$

volatilization

Hydrolytic Reduction of SiO_2

Obviously, volatilization of silica limits the oxidation protection capability of SiC by eliminating SiO_2 from the SiC surface . . . and the more water there is in the flame/environment, the faster SiO_2 is destroyed. Thus in 'wet' atmospheres or gas mixtures locally high in O_2 content, the SiC substrate is at risk, while in low or non-oxygen mixtures (or those under the reducing influence of H_2 gas), destruction and volatilization of the silica layer is imminent.

Now, in high temperature anhydrous environments which are also high in hydrogen H_2 content, both the oxide phase and the SiC substrate are susceptible to reductive degradation (etching) with the production of silane compounds and water or hydrocarbons, respectively . . .

$$\mathrm{SiO_2}\ (s) \quad + \quad \mathrm{H_2}\ (g) \xrightarrow{>\ \sim 3000^\circ\mathrm{F}} \mathrm{Si}_n\mathrm{H}_{2n+2}\uparrow \quad + \quad \mathrm{H_2O}\uparrow$$

volatilization

Reduction / Etching of SiO_2

$$\mathrm{SiC}\ (s) \quad + \quad \mathrm{H_2}\ (g) \xrightarrow{>\ \sim 3000^\circ\mathrm{F}} \mathrm{Si}_n\mathrm{H}_{2n+2}\uparrow \quad + \quad \mathrm{C}_n\mathrm{H}_{2n+2}\uparrow$$

volatilization

Reduction / Etching of SiC

In mixed environments containing varying partial pressures of O_2, H_2O and H_2, all three reactions can take place concurrently within the same general volume space but on different surface regions of the article. Of course, this situation is dependent on the particular propellant used, gas flow turbulence (or lack of it), temperature and pressure over time, and intermolecular gas interactions, as well as specific chemical/physical surface variations that already exist across the article itself. Any one of these factors, or more likely a combination thereof, can affect regional surface variations in the gas mixture composition as well as the distribution of localized thermal gradients, a combination of which will act to create domains or 'pockets' of varying composition and chemical activity.

Thus, the surface of an exposed or post-fired article may contain isolated spots or regions of degradation in which some were dominated by oxidation, some by hydrolysis and others by reduction. Also, due to the dynamic variation in localized gas compositions during a burn cycle or exposure event, the *timing* of each degradation process undoubtedly plays a role in the final appearance of a given anomaly . . . in some cases, a given region may be subjected to oxidation in the first half of the burn cycle and then reduction in the second half, or vise versa. This obviously makes it difficult to tell *what* the predominate degradation mechanism was since the effects of the second process may not only mask those of the first, but may alter identifiable characteristics of the first process beyond recognition, sometimes misleading or confusing the analyst.

As an example, the depleted oxygen environments in downstream gas mixtures of many solid rocket burn processes are known to contain partial levels of the following compounds which vary over the time cycle and most likely by specific location within the nozzle or chamber volume . . . (a) CO, which is one of the primary products of pyrolysis (burning without oxygen) or partial oxidation; **:**C=O may behave as a very weak oxidizing *or* a reducing agent, depending on the local influences; (b) HCl, which is a mild reducing agent (HCl gas is not acidic until it is solvated in water, and its solubility in water decreases with temperature; it is expected to be water-insoluble in flame environments); (c) H_2O, which can act as an oxidizer *or* a reducer, depending on the local influences (although it is a stronger oxidizing agent); (d) N_2, which is essentially inert, but in the presence of H_2, N_2 will be in gaseous equilibrium with ammonia NH_3, a strong reducing agent; (e) CO_2, which is a mild oxidizing agent; and (f) H_2, which can become very a strong reducing agent under the right conditions. In general, H_2O and CO_2 are the basic products of combustion (thermal oxidation) of organic materials (such as the binder in a solid fuel mixture). The presence of CO and H_2 imply that oxygen-starved pyrolysis or partial oxidation also occurred. This may have transpired concurrently with combustion, perhaps in isolated regions or asynchronously in time.

Intermolecular interactions in the gas mixture are probably influenced mostly by dipole-dipole attractions since CO, HCl, H_2O (and NH_3) all exhibit distinct dipole moments and may associate accordingly, as long as local turbulence and flow factors permit. In such regions, mild chemical reduction reactions are expected to dominate. Also, chemical effects in these regions might include minor side reactions possibly leading to the formation of nitrogen oxides, chlorinated oxides and more H_2. All in all, other than a few partially oxidized anomalies on surfaces here and there, these kinds of environments are expected to be dominated by reduction reactions. In general however, chemical degradation of surfaces may less-than-insignificant since these (depleted) environments are not very reactive in the first place.

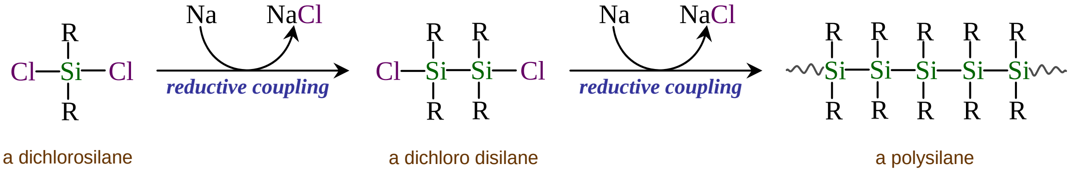
ALTERNATE IDEAS LEADING TO 1:1 SIC PRE-CERAMIC THERMOSETS

One of the major concerns with the current method for producing crosslinkable (thermoset) carbosilanes is the constant emission of flammable H_2 gas throughout storage, handling and processing of the resin, all the way until peak pyrolysis temperature when the material finally reaches it's initial green ceramic state. As illustrated earlier, silane-bound hydrogen atoms are readily liberated and then combine as H_2 is expelled from the non-ceramicized forms of these resins in almost all environments. Due to the tendency of silanes to dehydrogenate, almost spontaneously, it may be beneficial to consider occupying the substituent positions along the carbosilane chain with groups other than hydrogen, such as methyl and/or silyl itself. As illustrated on page 12, hydrogen generation is due heavily to reactions with moisture and oxygen which only need to be present in trace amounts as they are easily absorbed from shop atmospheres during transfers or the headspace in storage bins. Both of these reactants are nucleophiles toward electropositive silicon in silyl hydride molecules or segments. Conceivably, substitution of all the hydrogen positions in the Si–C system with other molecular groups could allow these substituents to act as blocking agents, eliminating the vulnerability and reactive susceptibility of these resins toward natural atmospheric constituents, as well as the undesirable and hazardous emission of hydrogen gas.

Another concern involves the efforts to maintain the Si:C stoichiometric balance in freshly synthesized product molecules. Depending on the level of aliphatic (allyl) crosslinking groups introduced into the polymer structure (about 10-15% for SMP-10), there is an obvious tendency to shift the Si:C balance in the carbon direction, possibly leading to the formation of carbon-rich ceramic end-products. In many applications, carbon-rich ceramics are acceptable, but in other cases, purely stoichiometric SiC may be of prime importance. Ultimately, the presence of carbon domains dispersed throughout the ceramic phase could conceivably lead to the formation of undesirable voids or macro-pores created when the carbon phase volatilizes during oxidation or hydrolytic exposures and excursions. For most electrical and semiconductor applications, stoichiometric SiC is crucial. Likewise, in high oxidation aerospace environments, undue levels of isolated carbon domains could become detrimental.

In analogy to the organic alkanes, silanes consist of sp^3 bonded structures which join Si–Si silicon atoms in sigma orbitals along the primary backbone. However, the strength of Si–Si sigma bond is only about 60% that of C–C sigma bonds. There is a long history and an unlimited number of compounds containing sp^2 double bonded carbon atoms C=C derived from the family of organics well known as the alkenes and dienes. Not too long ago, sp^2 hybridized π orbitals (double bonds) directly associated with Si were unheard of. However, there are now small but growing families of silicon-based compounds or functional groups centered around double bonded sp^2 silicon-silicon atoms Si=Si as well as sp^2-bonded silicon-carbon atoms Si=C, all generally referred to as the 'silenes'. More specifically, entities containing the Si=Si group are commonly classified as 'disilenes' and those containing Si=C can be identified as 'carbosilenes'. Unfortunately, both the Si=Si and Si=C bonded systems are short-lived species, which react instantly with atmospheric O_2 and H_2O . . . unless bulky side groups are attached to the two atoms, instead of hydrogen. Interestingly, the use of bulky substituents could also help reduce the level of hydrogen out-gassing. Special monomers containing these unsaturated functional groups could open the door to an array of novel techniques for producing improved, next generation pre-ceramics.

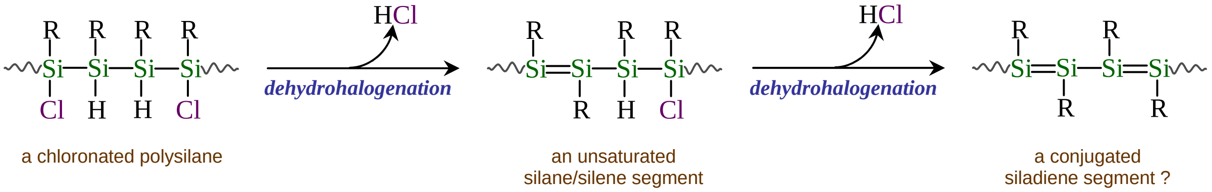
First however, recall that di-, tri- and polysilanes can be formed by reaction (reduction) of dichlorosilanes with an active metal such as sodium, via reductive coupling between silane units . . .



Method for the Synthesis of Polysilanes

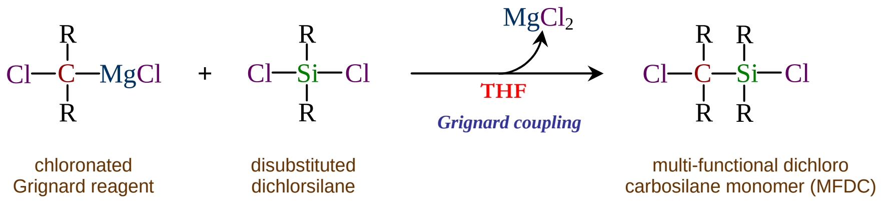
As with the silicones, R may be –Cl, –H, $–CH_3$, $–C_2H_5$, $–C_6H_5$ (aromatic), and even $–SiH_3$, $–SiH_2CH_3$, etc . . .

. . . and then unsaturated silenes can be (theoretically) generated by dehydrohalogenation of the appropriate (chlorinated) silane . . .

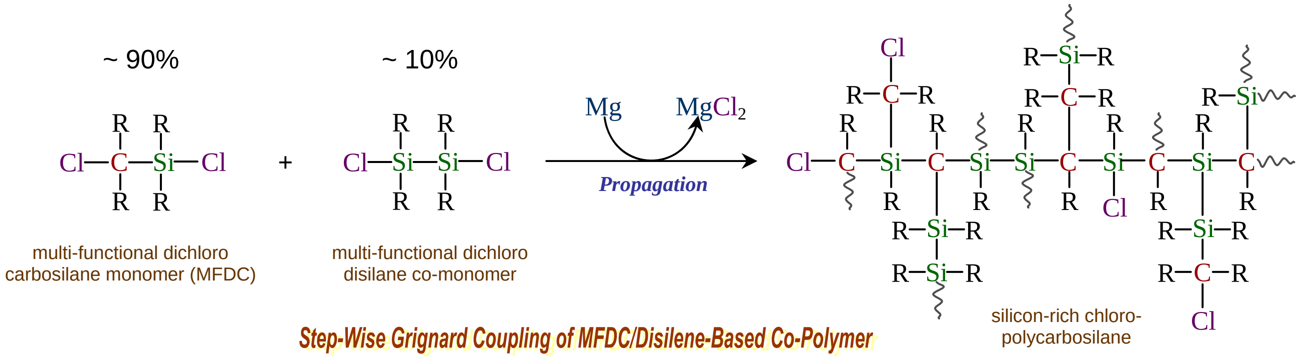


The following ideas are hypothetical, but they might be suggested as more than mere curiosities, possibly offering a starting point for potential or alternative solutions to some of the issues at hand. There are recent indications that some of these concepts are feasible, however, unsaturated compounds containing the Si=Si and Si=C groups are still in the their infancy. Improved and refined techniques are needed to stabilize these materials and to obtain better controls over their tendency to prematurely 'kick-off' (dimerize and crosslink), as well as their sensitivity to common industrial processing environments. From many perspectives, silenes are only transition state intermediates or very short-lived species. Nevertheless, one approach here could suggest potential modifications applied during the first stage of the carbosilane polymer synthesis process and another might look at similar concepts associated with the second stage when the crosslinking groups are normally incorporated into the polymer structure.

As covered earlier, Grignard techniques are likely pathways leading to formation of the primary monomer reactants and subsequent stepwise synthesis of the principal polymer backbone (reference page 7 of this paper). Here, the monomers are chlorinated methyl–silyl compounds and the polymerized product is a linear, but highly branched (dendritic) structure of alternating Si–C atoms. The monomer, monochloromethyl trichlorosilane (MMTS) was used as an illustrating example. In practice however, varying the substituents on both the carbon and silicon atoms leads to the use of more than one monomer in the reaction mixture to generate the desired polymer since the nature and quantity of constituents controls the reaction rates as well as certain secondary and tertiary structural features in the product. These attributes directly affect the extent of polymer branching as well as the degree of entanglement and chemical interactions (bonding) between branches. At the least, chloride groups are needed on both ends of the reactants in order for step-wise coupling to occur, and completely chlorinated reactants are extremely reactive and dendrite-forming. A controlled mixture of multi-functional monomers would be a preferred reactant base for creating the carbosilane structure of choice. Formation of a representative monomer can be illustrated by slightly modifying the reactions given on page 7 . . .



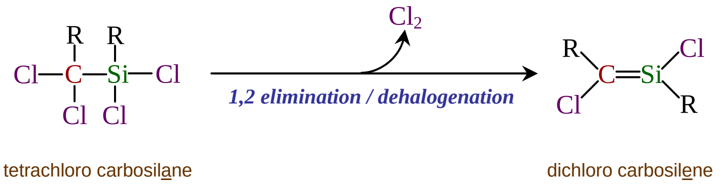
If these multi-functional monomers are allowed to react with *disilane* (as a co-monomer) during the step-wise polymerization process, the Si:C ratio could be shifted in favor of Si within the primary polymer backbone – before any aliphatic crosslinking groups are ever introduced into the structure . . .



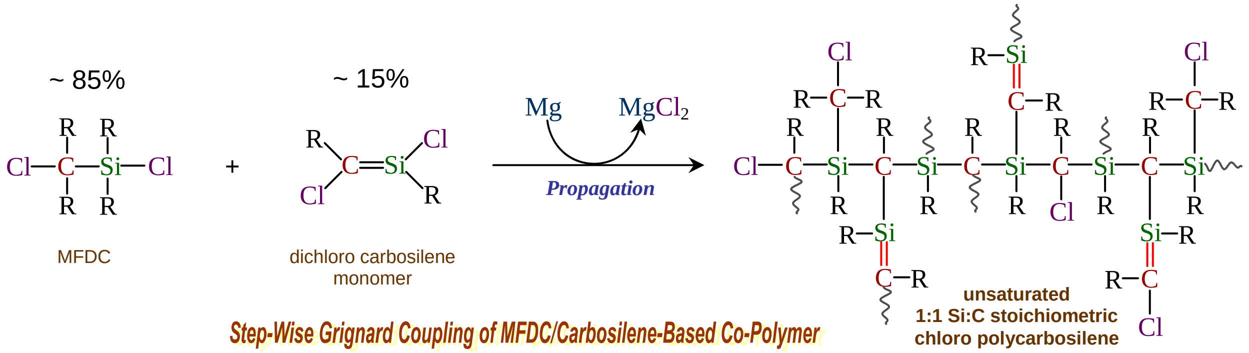
Step-Wise Grignard Coupling of MFDC/Disilene-Based Co-Polymer

This first stage polymer (a silicon-rich chloropolycarbosilane) can then be subjected to the appropriate reaction sequence for incorporating the allyl crosslinking groups into the structure as shown on pages 8 and 9. Attachment of these groups into the structure periphery via Grignard coupling (page 9) may be the preferred method, considering it's compatibility with the Grignard polymerization process employed for construction of the principal polymer backbone. Careful planning with this approach could establish a slight excess of silicon in the base polymer designed to appropriately counter-balance the carbon-rich crosslinking groups which would be added into the structure during the second phase.

Now, unsaturation functionality can also be introduced *directly into the polymer backbone*, minimizing the level of allyl crosslinking groups required in the second stage or possibly even eliminating the requirement for pendant crosslinking groups altogether. The appropriate carbosilene can be prepared by dehalogenating a modified version of the MFDC monomer via elimination . . .



The carbosilene can then be strategically incorporated into the reaction process as a co-monomer to establish unsaturation points (double bonds) into the primary branches of the structure . . .

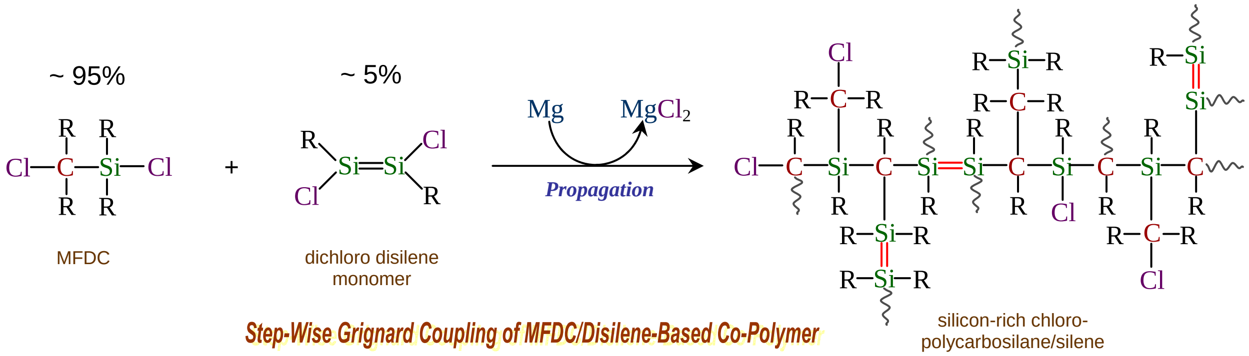


Step-Wise Grignard Coupling of MFDC/Carbosilene-Based Co-Polymer

In all examples, R may be –Cl, –H, $–CH_3$, $–C_2H_5$, $–C_6H_5$ (aromatic), and even $–SiH_3$, $–SiH_2CH_3$, etc . . .

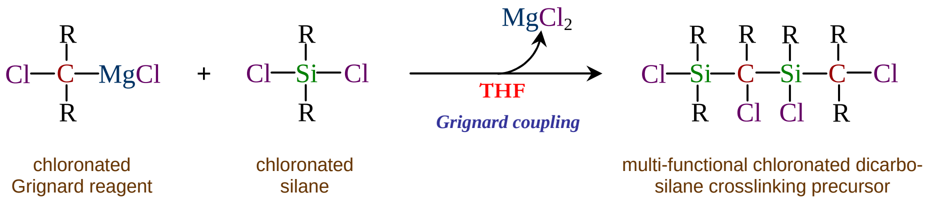
This single stage product may only need to be subjected to reduction/dehalogenation and drying operations before final preparations for packaging. The carbosilene C=Si bond is about 60% the strength of a typical alkene C=C bond. It can be stabilized by taking advantage of steric protection with bulky substituents and minimizing adverse tertiary structural effects. While C=C bonds are flat and rigid, the C=Si group is non-planar and (more) flexible. Additionally, because of the difference in electronegativities between C and Si, both the C–Si and C=Si bonds are polar with the Si atom becoming electropositive δ^+ and C atom negative δ^- (these are not symmetrical bonds as with C=C since the outer *s* and *p* orbitals in the Si atom are larger and farther away from the nucleus that those in the C atom). Consequently, this leaves the Si open to attack by nucleophillic agents, such as water, alcohols, carbonyls, oxygen, etc...

A combinational approach could incorporate a few unsaturated Si=Si units into the base polymer by using a disilene Si=Si as co-monomer. This would reduce the level of subsequent crosslinking groups required *and* counter-balance the slight excess of carbon incorporated during the second stage . . .



Step-Wise Grignard Coupling of MFDC/Disilene-Based Co-Polymer

In an analogous approach, any one or more of these techniques could be applied to modify the actual crosslinking agent itself (propene) prior to second stage reactions (see the Grignard reaction on page 9 for reference). However, as an alternative to these modifications, consider again the reactions pertaining to the basic monomer (MMTS) shown on page 7 and at the top of page 21 above (MFDC), only this time, the dimer, a chlorinated dicarbosilane, is isolated as the new crosslinking precursor agent . . .



R may be –Cl, –H, $-CH_3$, $-C_2H_5$, $-C_6H_5$ (aromatic), and even $-SiH_3$, $-SiH_2CH_3$, etc . . .

Using methods which have already been described, the dicarbosilane can be subjected to dehalogenation, converted into the appropriate Grignard agent and then attached to polymer end segments analogous to the reactions shown on page 7. With this approach, the crosslinking groups are comprised of carbosilane/silene units, which accomplish two objectives . . . they include unsaturated groups for crosslinking purposes *and* they maintain a near perfect 1:1 Si:C ratio, regardless of the number of crosslinking groups incorporated. If this method were feasible, the synthetic chemist could strategically design and custom-tailor a thermosetting, stoichiomentic SiC precursor using as many or as few crosslinking groups as desired to meet any specific processing and performance requirements . . .