Silvia Adriana Collins Abarca

SYNTHESIS OF HYBRID ORGANIC-INORGANIC POLYMER

Tese submetida ao Programa de Pós Graduação em Engenharia Química da Universidade Federal de Santa Catarina para a obtenção do Grau de Doutora em Engenharia Química.

Orientador: Prof. Dr. Ricardo Antonio Francisco Machado

Coorientador: Prof. Dr. Günter Motz

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Synthesis of Hybrid Organic-Inorganic Polymer

por

Silvia Adriana Collins Abarca

Tese julgada para obtenção do título de **Doutor em Engenharia Química**, área de Concentração de **Desenvolvimento de Processos Químicos e Biotecnológicos** e aprovada em sua forma final pelo Programa de Pós-Graduação em Engenharia Química da Universidade Federal de Santa Catarina.

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Prof. Dr. Ricardo Antonio Francisco Machado
orientador

____
Prof. Dr. Ricardo Antonio Francisco Machado
coordenador

Banca Examinadora:

____
Prof^{a}. Dr^{a}. Claudia Sayer

____
Prof. Dr. Leonel Teixeira Pinto

____
Prof. Dr. César Vitório Franco

____
PhD. Samuel Bernard

____
Prof. Dr. rer. nat. Günter Motz

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To my beloved parents for all the love and support.

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We cannot hope to build a better world without
improving the individual. Toward this end, each
of us must work for his own highest development,
accepting at the same time his share of
responsibility in the general life of humanity—our
particular duty being to aid those to whom we
think we can be most useful.
(1937 - Marie Sklodowska Curie - Celebrating the
100th Anniversary of Madame Marie Sklodowska
Curie’s Nobel Prize in Chemistry)

I am among those who think that science has great
beauty. A scientist in his laboratory is not only a
technician: he is also a child placed before natural
phenomena which impress him like a fairy tale.
We should not allow it to be believed that all
scientific progress can be reduced to mechanisms,
machines, gearings, even though such machinery
has its own beauty.
(1933 - Marie Sklodowska Curie - Celebrating the
100th Anniversary of Madame Marie Sklodowska
Curie’s Nobel Prize in Chemistry)

RESUMO

O desenvolvimento de novas tecnologias e equipamentos na área de engenharia exige a adaptação dos materiais hoje empregados ou criação de novas matérias primas capazes de suportar os mais diversos ambientes e condições. Durante anos a engenharia química e de materiais vem estudando os materiais inorgânicos como moléculas precursoras com o intuito de obter, após tratamento térmico, fibras ou cerâmicas de alta performance, dotadas de características químicas e térmicas inalcançáveis com outros materiais. Materiais cerâmicos são destinados à aplicações bastante nobres na área aeroespacial e automotiva devido ao elevado custo dos compostos empregados em sua obtenção.

Com o objetivo de produzir materiais com características melhoradas, aumentando assim o leque de aplicações e ao mesmo tempo reduzir os custos de produção, buscou-se introduzir moléculas orgânicas ao processo de síntese. A inserção de compostos orgânicos permite a inclusão de funções orgânicas, melhora as propriedades químicas, permite o uso de menores quantidades de material inorgânico e diversifica a área de aplicações. Até o presente momento, diversos autores sintetizaram novos compostos híbridos orgânico-inorgânicos através de rotas sintéticas variadas. Neste trabalho foram utilizados precursores inorgânicos comerciais e o monômero orgânico estireno através de duas grandes rotas sintéticas, polimerização em solução via radicais livres e hidrossililação assistida por catalisador metálico com adição de iniciador radicalar.

Produtos com diferentes características foram sintetizados por ambas as técnicas. Ambas as técnica utilizadas mostraram-se adequadas para a obtenção de um polímero híbrido com as características desejadas. O híbrido orgânico-inorgânico sintetizado apresentou elevada estabilidade térmica resultando em um alto grau de ceramização, caracterizando-o assim como um bom material precursor para cerâmicas.

Palavras-chave: Polímeros híbridos, Hidrossililação, Polimerização em solução.

ABSTRACT

The development of new technologies and equipment in engineering area forces the improvement of materials used nowadays or the conception of new with capability to be applied in different environments and conditions. Along years chemical and material engineers have been studying inorganic materials as precursor molecules intending to obtain, after thermal treatment, high performance fibers and ceramics, with singular chemical and thermic characteristics obtained only by these materials. Ceramic materials are applied in noble applications like aerospace and automotive due to the high aggregate value of raw material.

A promising material with improved characteristics, to increase the range of applications and decrease production costs, is the combination of organic molecules and preceramic compounds in a synthesis process. The addition of organic compounds allows the inclusion of organic functions, improves chemical properties, reduces the amount of inorganic material and diversifies the application area. Nowadays several authors have synthesized new hybrid organic - inorganic compounds by numerous synthetic routes. In this work commercial inorganic precursors and organic styrene monomer were reacted by two synthetic routes, solution polymerization with free radical initiator and hydrosilylation assisted by metal catalyst with the subsequent addition of free radical initiator.

Products with different characteristics were synthesized using polymerization by free radical initiator and hydrosilylation followed by radical initiator addition. Both techniques revealed to be satisfactory to obtain a hybrid polymer with improved characteristics. The new organic-inorganic hybrid materials synthesized showed high thermal stability resulting in a high ceramic yield, characterizing it as a good precursor material for ceramics.

Keywords: Hybrid polymers, Hydrosilylation, Solution Polymerization

FIGURE LIST

Background

Experimental Methodology and Materials

Results and Discussion

TABLE LIST

Background

Experimental Methodology and Materials

Results and Discussion

SCHEMES LIST

ABREVIATIONS AND ACRONYMS

ABSE	Polysilazane Precursor
AIBN	Azobis(isobutyronitrile)
BPO	Benzoyl Peroxide
cBN	Cubic Boron Nitride
DCP	Dicumylperoxide
DVB	Divinylbenzene
DSC	Differential Scanning Calorimetry
D4	Octamethylcyclotetrasiloxane
FTIR	Fourier Transformed Infrared
GPC	Gel Permeation Chromatography
HTT 1800	Polysilazane Precursor
MATPMS	Methacryloxy-propyl-trimethoxysilane
MGy	MegaGray
ML 33	Polysilazane Precursor
Mw	Molecular Weight
NMR	Nuclear Magnetic Resonance
PCS	Polycarbosilane
PDC	Polymer-derived Ceramic
PDMS	Polydimethylsiloxane

CONTENTS

1. INTRODUCTION

Hybrid organic-inorganic materials represent nowadays one of the most important compounds to be applied in a range of areas. It is extensively known the difficulty to obtain desired characteristics in a single compound. The combination of organic and inorganic properties can represent an alternative to the manufacturing of new materials.

Hybrid organic-inorganic materials present excellent thermal, optical and mechanical properties, obtained through the combination of the high thermal and chemical stability of inorganic compounds with the processability and flexibility of organic compound (José and Prado, 2005). Although, the synthesis of a hybrid structure or even blended hybrid compounds continues to be a challenge to researchers. Those synthesis procedures require profound knowledge in organic and inorganic material synthesis and techniques. However due to the noble application of hybrid materials as precursors of high performance ceramics to automotive and aerospace industry represents a great motivation to develop new synthesis routes and compounds.

An interesting and relatively new research topic, which is extensively studied nowadays, is the polymer-derived ceramic (PDC) technology. A number of works about high temperature stable polymer-derived ceramics were published. First assignments about non-oxide ceramics synthesized by precursors were made by Ainger and Herbert and at the same time by Chantrell and Poppers in 1960s (Riedel et al., 2006). Although, the transformation of polysilazanes, polysiloxanes and polycarbosilanes to ceramic materials was performed only in 1970s by Verbeek and coworkers (Riedel et al., 2006). Yajima et al. (1975) can be cited as one of the first authors to investigate the use of polycarbosilane precursor to obtain SiC ceramics, the Yajima process.

Riedel et al. (2006) published an interesting review about silicon-based polymer-derived ceramics presenting synthesis techniques and applications. Silicon-based polymeric precursors were proven to be excellent material for the development of technologically important ceramic components such as fibers, coatings, infiltrated porous media and complex bulk parts. These results are an important motivation to further significant improvements of their chemistry, synthesis, processing and properties.

Nevertheless the development of PDCs was restricted to the synthesis of precursors using inorganic molecules. Intending to improve the application possibilities, to synthesize new molecules with peculiar characteristics and to apply lower quantities of inorganic compounds, two different synthesis routes were applied to react an organic monomer with inorganic precursors. The inorganic precursors used were already studied as ceramic precursor by coworkers of Universität Bayreuth and presented a high thermal stability and good ceramic yield.

2. OBJECTIVE

The main goal was to obtain a hybrid organic-inorganic polymer with high thermal stability and good ceramic yield, to work as a polymer-derived ceramic.

2.1 SPECIFIC OBJECTIVES

- Synthesize hybrid organic-inorganic polymer using Styrene as organic monomer and HTT 1800 as inorganic precursor;
- Describe synthesis mechanisms involved;
- Synthesize organic-inorganic polymer using Styrene as organic monomer and HTT 1800 as inorganic precursor by hydrosilylation reaction;
- Synthesize organic-inorganic polymer using Styrene as organic monomer and ML 33 as inorganic precursor by hydrosilylation reaction.

3. BACKGROUND

3.1 POLYMER DERIVED CERAMICS

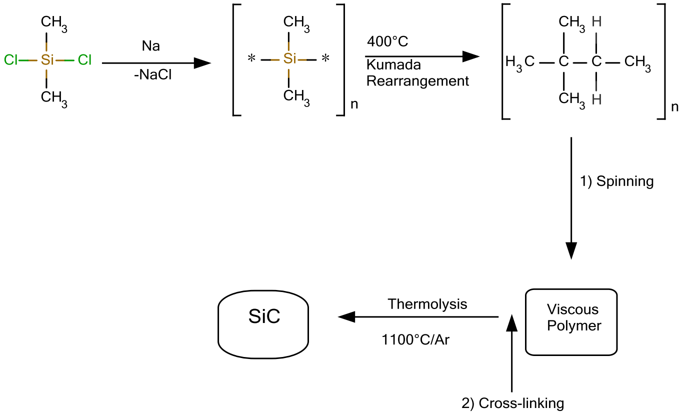
For many years ceramics have been used, from general products of house care until raw material for construction. In the last decades some different potential for ceramic materials was observed with the development of products with higher aggregated value e.g. substrates for electronic devices, sensors, bioceramics, cutting tools, glow plugs and raw material for aerospace equipment (Riedel and Dressler, 1996) .

It is known that simple inorganic compounds are not the best option to apply at high temperatures once those materials present some limitations related to mechanical properties (Kroke et al., 2000). Due to those undesired characteristics, studies about ceramics started.

According to Hennicke (1967), ceramic is a part of technologic chemistry, usually inorganic, nonmetallic compounds with low solubility on water and at least 30% crystalline (Traßl, 2001). Ceramics can be prepared and molded by applying a high temperature treatment. Another definition was presented by Kingery (1976) were all inorganic and nonmetallic materials are ceramics. Ceramics are principally based on ionic and covalent bonds as oxides, nitrides, carbides und borides (Traßl and Ro, 2002).

High performance ceramics formed by Si-C-N are materials with high strength and hardness, low thermal expansion coefficient and good oxidation resistance (Traßl et al., 2000).

The production of non-oxide ceramics starting from molecular precursors was reported in 1960s by two groups of authors, Ainger and Herbert, Chantrell and Popper (Riedel et al., 2006). However was just in 1970’s Verbeek, Winter and Mansmann developed the first practical transformation of polyorganosilicon compounds (polysilazane, polysiloxane and polycarbosilanes) to ceramic material (Riedel et al. 2006). It is unknown if it was Fritz or Yajima (or both at the same time) who performed the first synthesis of a SiC ceramic material from polycarbosilane precursors. However, this development results in the Yajima process (Equation 3.1 shows a simplified scheme) for the synthesis of SiC ceramic materials by the thermolysis of polycarbosilanes.



(3.1)

Adapted (Riedel et al, 2006)

According to Colombo et al. (2010) the polymer precursors represent inorganic/organometallic systems that provide ceramics with tailored chemical composition and a defined nanostructural organization by proper thermal treatment (curing and thermolysis process) under a controlled atmosphere. Polymer-derived ceramics (PDC) are also additive-free ceramic materials which can present an excellent oxidation and creep resistance up to exceptionally high temperatures.
The best known PDCs systems are displayed in Table 3.1.

Table 3.1 – Polymer-derived ceramic systems.

Binary system	Ternary System	Quaternary system
Si_3N_4	SiCN	SiCNO
SiC	SiCO	SiBCN
BN	BCN	SiBCO
AlN	----	SiAlCN
----	----	SiAlCO

Ceramic materials are mostly produced via powder metallurgical process, using sintering aids and/or through consolidation of covalent material at high temperature (up to 2000°C) and high pressure. In the case of the PDCs route starting from preceramic polymers, ceramic fibers, layers, or composite materials can be produced, which cannot be easily obtained using the powder technology (Colombo et al., 2010).

A range of methodologies can be used to process or shape preceramic polymers since conventional polymer-forming techniques, e.g. polymer infiltration pyrolysis (PIP), injection molding, coating using a solution, extrusion and resin transfer molding (RTM). To obtain the ceramic product, the processed polymer needs to be heated to high temperatures to consolidate the elements into the structure to a ceramic.

It is possible to achieve higher thermal-mechanical stability when a precursor-derived covalent ceramic is used. Some properties as creeping, oxidation, crystallization, or phase separation can be influenced.

A significant quantity of studies on silicon–based polymers has been made to search for different and improved synthesis routes of preceramics polymers. A range of different materials with desired properties can be processed to important technological applications as fibers, coatings, infiltred porous substrates or complex-shaped bulk parts (Riedel et al. 2006). Many studies of polysilanes, polycarbosilanes, poly(organosilazanes) and polysiloxane can be found in literature.

PDCs present a relatively low synthesis temperature (1100°-1300°C) when compared to classical ceramic powder processing technology (1700°- 2000°C or more). Due to these characteristics, PDCs have been extensively studied in the last few years.

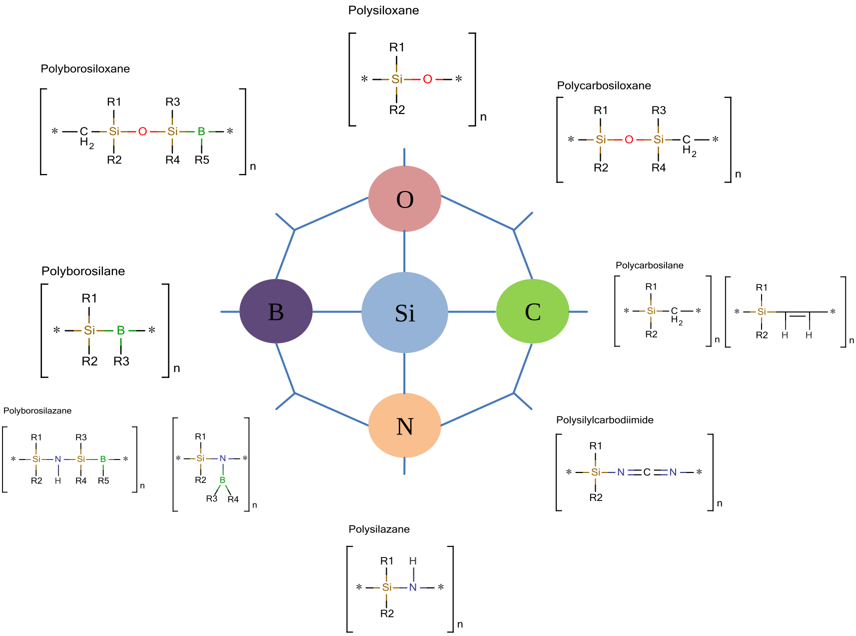
An efficient pyrolysis and consequently efficient ceramic is obtained by using a suitable polymer precursor, an adequate synthesis route and comprehensive polymer characterization. Adequate pyrolysis resulting in a high ceramic yield. Molecular design of PDC can be adjusted according macroscopic chemical and physical properties of precursor, resulting in a wide range of structures.

The ceramic yield is measured by the weight of ceramic product (percentage) related to the percentage of the starting material. The properties of this ceramic are related to its composition, structure and processing conditions and is reflected in the composition product, the amount and character of voids and cracks, the existence or nonexistence of grain structure for one or more phases present, and, if present, the distribution of multiple phases in terms of size and location (Wynne and Rice, 1984).

PDCs can be synthesized at low temperatures, although a complete pyrolysis and transformation of the silicon-based polymer to ceramic occurs at or below 1100°C (Seyferth and Plenio, 1990).

According to Colombo et al. (2010) to synthesize an organosilicon ceramic precursor (Figure 3.1) two important parameters should be considered to design the preceramic compound on molecular level: firstly, the group (X) or the polymer backbone and, secondly, the substituents R^1 and R^2 attached to silicon. The variation of (X) results in different classes of Si-based polymers. Functional groups R^1 and R^2 at the silicon atoms are responsible for thermal and chemical stability, solubility, electronical, optical and rheological properties.

Figure 3.1 - Preceramic organosilicon polymers (adapted).



Adapted (Colombo et al., 2010)

3.2 INORGANIC POLYMERS

Inorganic polymers represent an important segment of available materials for industrial applications. Nowadays they are considered a need to supplement conventional systems for polymers containing inorganic elements. Silicon is the second most widely present element in the earth’s crust (27.2% by weight). Also due to the properties conferred by silicon to inorganic molecules, makes sense to look for alternative polymer systems based on silicon atoms. Some of the most important molecular precursors will be presented in this chapter.

3.2.1 Si-Si molecular precursor

Polysilanes are composed by Si-Si bonds in the main backbone and organic substituents linked to the Si atoms. They have various features including photoconductivity, luminescence and most importantly, the thermal stability (Miller and Michl, 1989). However this structure can be modified to synthesize SiC precursors by the thermal reorganization of a polymethylsilane to yield the polycarbosilane using the Kumada rearrangement (Colombo et al., 2010).

Iwahara et al. (1990) synthesized alternating ethynylene-disilanylene copolymers. Acetylenic hydrogens of 1,2-diethyldisilanes were protonated by n-butyllithium to form dilithium species. These lithium compounds were reacted with 1,2-dichlorodisilanes to form the ethynylene-disilanylene copolymers in high yields.

Abu-eid et al. (1992) prepared a polysilane using sodium dechlorination, $CH_3C_8H_{17}SiCl_2$ was refluxed in toluene and reacted with sodium and 2-propanol. A high ceramic yield was observed for $[CH_3SiC_6H_5]_n$ and $[CH_3SiH]_n$.

Bushnell-Watson et al. (1996) prepared polymeric polysilane precursor for silicon carbide ceramics and fibers through Wurtz synthesis. Basically copolymers were synthesized by the dechlorination of methylphenyldichlorosilane and phenyltrichlorosilane using sodium metal dispersed in xylene. Authors concluded that variation in the solvent used to separate the reaction products modified their yield and characteristic properties. Molecular weight distribution also changed affecting directly the processing of ceramic fibers from these precursors. Ceramic yield suffered just small variation.

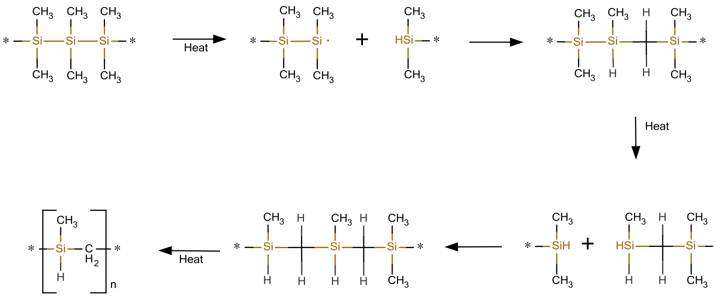
3.2.2 SiC

SiC are formed by a silicon-carbon polymer backbone. During many years they have been used successfully as ceramic precursor for polycarbosilanes. Depending on the structure of the carbosilane chain, different properties can be obtained. Currently the most studied research line focuses on the area of the Si-C fibers (Colombo et al., 2010). These fibers are used in metal, ceramic, and polymer matrix composites, being very effective at high temperatures. Some starting materials for obtaining these compounds are polycarbosilane (PCS) $[MeHSiCH_2]$ and polymetalcarbosilane (PMCS) (M = Ti, Zr and Al). A great number of studies in progress intend to synthesize new molecules to use carbosilane as polymer precursors.

Bouillon et al. (1991) studied ceramic properties of ten different functionalized polycarbosilanes or polycarbosilazanes precursors prepared from chlorinated poly(dimethylsilylene)methylene reactants. Authors observed that a linear structure does not lead to a high amount of inorganic residue by pyrolysis under argon pressure of 1 atm. This behavior is expected once, under these conditions, the linear polymeric chain is progressively broken into short fragments that give rise to an evolution of species with a low boiling point. To avoid this problem it is suggested to submit polymers to a cross-linking treatment (thermal or chemical) before pyrolysis, intending to increase ceramic yield. This step was firstly observed by Yajima on his route to PCS fibers. With this crosslinking step it is expected to obtain strong chemical bonds within the precursor polymer (Si-O or Si-N bonds). From those results it is clear that precursors with a high percentage of organic carbon do not necessarily lead to ceramics with a high percentage of free carbon. The most important point is the thermal stability of hydrocarbon linkages into the precursor. Another important characteristic is the ability to build a three dimensional polymeric network at the beginning of pyrolysis.

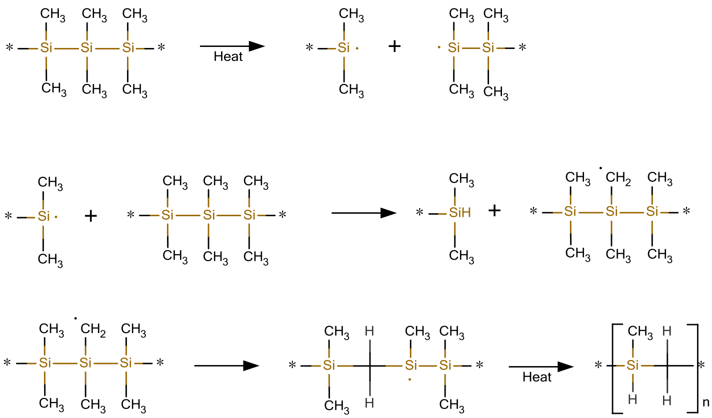
Nangrejo et al. (2000) developed a new method to obtain silicon-carbine-silicon nitride composite foams using preceramic polymers. Initially a polysilane was synthesized by the alkali dechlorination of a combination of chlorinated silane monomers with molten sodium. The polysilane precursor was dissolved in dichloromethane to form a polymeric precursor solution. Then Si_3N_4 powder was added to the solution with small pieces of polyurethane sponge. The product was pyrolysed, firstly at 900°C and subsequently at different ending temperatures (1100-1600°C). Polymeric precursor was converted to SiC and SiC-Si_3N_4 composite foams. The ceramic composite foam obtained showed well-defined open-cell structures. The increase of final temperature resulted in an increase of weight loss and shrinkage.

Yajima et al. (1975) worked during a long period synthesizing silicon carbide fibers with high tensile strength. In 1975 dimethyldichlorosilane with lithium catalyst was used as starting material to obtain dodecamethylcyclohexasilane. The product with high molecular weight was separated from a fraction with low molecular weight by using a solvent. The high molecular weight (Mw) fraction was suitable to produce fibers. A thermal treatment from room temperature to 1000°C was executed on fibers for 2 hours. It was obtained a black and metallic luster fiber with 60 % weight of ceramic yield. In the same year another article was published about the structural analysis of silicon carbide fiber. Through thermogravimetric analysis was observed initial decomposition at 300 °C and final decomposition at 800 °C with 60 % of residue. This behavior suggests that the polysilane was converted into polycarbosilane. Yajima et al. (1976) executed a new synthesis route using metallic sodium to dechlorinate dimethyldichlorosilane obtaining polydimethylsilane. The product was treated at 400 °C in inert gas to obtain a meltable polycarbosilane polymer. Pyrolysis was characterized by break up of organic bonds, such as Si-CH_3 and C-H during heating up to 1500 °C, which converted the polycarbosilane to continuous SiC fiber. Therefore, almost 60% of the material by weight was left. In 1978 Yajima et al. (1978) developed a new synthesis route of silicon carbide fibers using dimethyldichlorosilane as starting material and metallic sodium in xylene under N_2 atmosphere. Then polyborodiphenylsiloxane was mixed with polydiphenylsiloxane and reacted for 6h at 350 °C. It was obtained a polycarbosilane PC-1 with 48.8 % weight yield and PC-2 with 58.8 % weight yield. Yajima et al. (1978) also described the synthesis of silicon carbide fiber where a polycarbosilane play the role as precursor. First of all was synthesized an insoluble (in ordinary solvents) polydimethylsilane from metallic sodium and dimethyldichlorosilane (yield 88.7%). The polydimethylsilane was then pyrolysed at different temperatures. Yajima et al. (1978) suggest the mechanism for the formation of polycarbosilane by the thermal decomposition of polydimethylsilane (based on the thermal decomposition of hexamethyldisilane and methoxydisilane), presented in Equations 3.2 – 3.4.



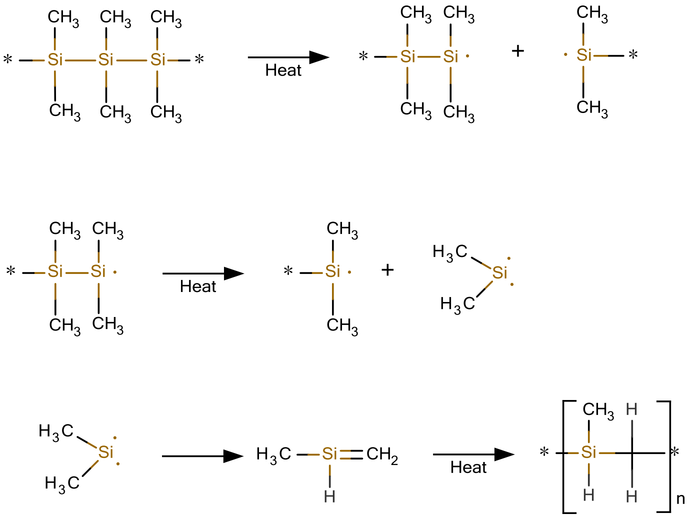
(3.2)

Radical transition reaction:



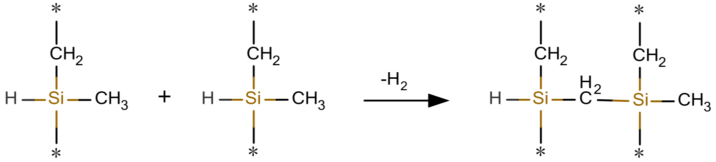
(3.3)

Further formation of dimethylsilene is possible:

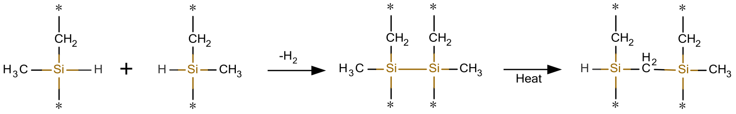


(3.4)

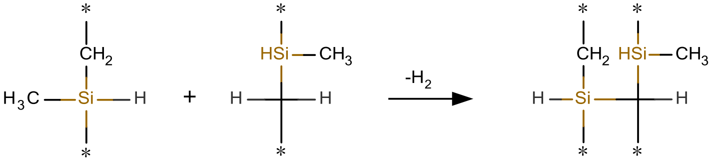
Those are just a part of possible reactions. It is also expected chain transfer reactions and ring formation. The reactions (Equations 3.2, 3.3 and 3.4) are responsible for the beginning of carbosilane formation and reactions in equations 3.5, 3.6 and 3.7 to the increase of molecular weight.



(3.5)



(3.6)



(3.7)

It is known that Si-H bonds play an important role when the polysilapropylene, as produced in the thermal decomposition of polydimethylsilane, increases the molecular weight and promotes polymerization reactions. Yajima et al. (1978) concluded that the increase of polymerization temperature (observed by the reduction of Si-H bonds) resulted in large amounts of ladder-bonds structures and consequently increase of cross-linking. As consequences appears the rigidity of molecular chain and rise in softening point.

Seyferth et al. (1996) studied the synthesis of $[CH_2CH(SiH_3)]_n$ through the reduction of poly(vinyltrichlorosilane) with lithium aluminum hydride to use as preceramic polymer. It was observed a moderate ceramic yield. Author suggests as an alternative to improve ceramic yield the crosslinking of preceramic compound with metallocene derivatives giving a soluble polymer whose pyrolysis in argon gave substantially improved yield of ceramic residue. This residue is composed of silicon carbide together with 10-13 wt % of free carbon.

Kowalewska et al. (2009) studied the formation of a new silsesquioxane compound, which present a carbosilane sterically hindered, resulting in a carbosilane-silsesquioxane. Carbosilane dendrimers with central Si_8O_{12} unit were prepared by building up the carbosilane arms in consecutive hydrosilylation/vinylation steps. Silsesquioxane molecules were surrounded by carbosilane groups, using reactive trialkoxysilane as precursor. The hybrid material was found to be hydrophobic and extremely thermally resistant. It was observed, at 700 K (427.8 °C) only about 5% weight loss during thermal analysis under nitrogen atmosphere. No sublimation was observed during heating and a substantial char residue (approximately 30%) at 1100 K (826.8 °C).

Tögel et al. (1996) studied the thermal properties of polycarbosilanes formed by the pyrolysis of some molecules as $SiMe_4$, Me_3SiCl, Me_2SiCl_2 and $(Me_2Si\text{-}CH_2)_n$. It was found that the yield of high molecular weight carbosilanes obtained from pyrolysis decreased with the increase of the number of methyl groups of the starting compound. High molecular weight carbosilanes are formed by condensation via Si-C links of cyclic and oligocyclic compounds, however between 1000 and 1500 °C the ceramic yield decreases to a low value. Therefore, the polycarbosilanes formed are not suitable precursors for the formation of SiC.

Idesaki et al. (2001) synthesized a SiC fiber from polycarbosilane-polyvinylsilane (PVS) blend polymer with electron beam curing under vacuum. The blend polymer was prepared by freeze-drying of a benzene solution in vacuum. Using a small batch melt-spinning the fiber was obtained. The yield was estimated from the weight ratio of the SiC fiber to the as-spun polymer fiber. The yield of the SiC fiber from PCS-20% PVS increased from 73% for the curing dose of 15 MGy to 80% for 35 MGy, while the yield from PCS was almost constant at about 82% (even by different curing doses). This yield difference between PCS-20% PVS (curing dose of 15 MGy) and PCS can be attributed to the presence of a low molecular weight component (not cross-linked) whose intend to evaporated during the pyrolysis process. The increase of PCS-20% PVS yield to 80% is due to sufficient cross-linking of PVS molecules.

Li et al. (2008) studied the effect of the polycarbosilane structure on final ceramics yield. Using Grignard coupling of chloromethylmethyldichlorosilane, chloromethyltrichlorosilane and allyl chloride, followed by reduction with lithium aluminium hydride a liquid polycarbosilane was synthesized. Highly branched polycarbosilanes were preferred at the beginning of structural design in order to avoid great oligomers loss. It was obtained as product highly branched structures. No obvious weight loss below 300 °C was observed. The ceramic yield obtained was around 70 wt%.

Yang et al. (2012) prepared a SiC fiber containing yttrium using yttrium-acetylacetonate to introduce traces of yttrium as a sintering aid was synthesized according the process developed by Yajima et al. (1976).

3.2.4 SiO

Si-O is the molecular precursors used to obtain polysiloxanes which have the main backbone formed by links alternating Si-O-Si-O atoms. Present excellent chemical, physical and electrical properties (Abe and Gunji, 2004). Those compounds promote high thermal stability, which cannot be obtained by the most organic polymers. Two of the most attractive characteristics of polysiloxanes are the low surface tension and low glass transition temperature.

Park et al. (2004) synthesized a poly(imide)siloxane precursor in a range of compositions and evaluated the ability to form carbon membranes containing silica. The imide group present in the molecule was transformed during pyrolysis in a carbon-rich phase, which has the ability to work as a molecular sieve for gas mixtures such as H_2/N_2, He/N_2, and CO_2/N_2 O_2/N_2. The siloxane chains are converted into a silica-rich phase and influence the gas permeation characteristics of the C-SiO_2 membranes. It was observed by Park et al. (2004) that the gas separation properties of C-SiO_2 membranes depend on the polydimethylsiloxane (PDMS) content and the siloxane chain length in the imide siloxane precursor. PDMS with longer siloxane chain length for the same volume fraction of PDMS in the precursor resulted in a drastic increase in gas permeability.

Blum et al. (2005) used polyhydridomethylsiloxane (PHMS) to synthesize and characterize a carbon-enriched silicon oxycarbide. PHMS was mixed with vinylmethyltetracyclomer and a Pt catalyst. The solution was allowed to stand overnight at room temperature for curing. Pt catalyst was mixed with divinylbenzene and PHMS and cured. It was obtained a highly crosslinked cured material by employing the hydrosilylation reaction without incorporation of additional oxygen into the cured precursor. The very efficient crosslinking resulted in very high ceramic yields (over 80%). The ceramic yield only decreases when divinylbenzene (DVB) exceeds to 60 wt% of PHMS. Up to 60 wt%, the reacted DVB predominantly bonds to two silicon atoms and serves as a crosslinking unit. Further increase of the reagent results in a significant fraction of DVB as pendant groups or self-polymerized, no longer serving as crosslinking unit.

Nyczyk et al. (2012) executed the crosslinking between linear polysiloxanes containing vinyl groups (previously prepared by ring opening polymerization) with hydrogensiloxanes (crosslinking agents) using hydrosilylation techniques. 1,3,3,5,5-Pentamethyl-1-vinylcyclotrisiloxane and 1,3,5-trimethyl-1,3,5-trivinylcyclotrisiloxane were the monomers used to prepare by kinetically controlled ring opening polymerization both polymers used, D_2V and V_3 respectively. Subsequently was performed the hydrosilylation with different cross linking agents using platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt´s catalyst). It was observed that hydrosilylation of linear polysiloxanes with vinyl groups along the chain with hydrogensiloxanes differing in functionalities and molecular structures leads to the formation of polymer networks in which unreacted functional groups remain. The amount of unreacted functional groups in the system depends on functionality and molecular structure of hydrogensiloxane applied. The quantity and localization of vinyl groups affect the extent of hydrosilylation process.

Sorarù et al. (2012) developed new polysiloxane and polycarbosilane aerogels via hydrosilylation using preceramic polymers as starting materials. Polyhydridomethylsiloxane (PHMS) is cured with 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (TMTV) and a polycarbosilane (PCS) is crosslinked with divinylbenzene (DVB). Reactions were performed in the presence of a platinum catalyst, platinum-divinyltetramethyldisiloxane complex. It was formed a colloidal aerogel with meso and macropores. The particle size, pore size and total pore volume of the aerogels PHTV (PHMS cured with TMTV) increased with the solvent content of the starting solution. For PCDV (PCS with DVB) samples the microstructure did not change significantly with the increase of solvent amount. Was observed also a small increase in the pore size with the increase of Si-H/C=C molar ratio.

3.2.4 SiN/SiCN

Polysilazanes backbones are formed basically by alternated Si-N bonds with pendant carbon-containing groups. Those compounds have been extensively used as precursors for silicon carbonitride ceramics. With this material is possible to obtain SiCN ceramics for high temperature application and special thermal, mechanical and electrical properties.

First reports about the synthesis of SiCN materials by using silazanes are from the 1960 years (Colombo et al. 2010). Silazane compounds can be found as cyclic molecules (Kroke et al. 2000) and are usually used as precursors for the preparation of ceramics via pyrolysis of liquid, vapor and solid phases.

One of the earliest synthesis methods was reported by Rochow (1966), which promoted the synthesis of poly(organosilazane) by ammonolysis of chlorosilane. Verbeek (1973) developed ceramic fibers with small diameter from carbosilazanes (Colombo, 2010b).

High performance ceramics can be obtained through high molecular weight polymers. For this reason some methods have been developed to increase molecular weight and the degree of cross-linking (Colombo et al., 2010). Laine (1988) used a transition metal complex in the presence of silazane oligomers to increase the degree of cross-linking, resulting in a strong polymer composite.

Glatz et al. (2010) synthesized a copper aminopyridinate (Cu @ SiCN) used to perform a metal modification of commercial polysilazane HTT 1800. $CuBr_2$ was reacted with lithiated (4-methylpyridin-2-yl)trimethylsilanylamine. One of the complexes obtained was employed as a transmetalation agent in a reaction with HTT 1800 (AZ Eletronic Materials, Wiesbaden, Germany). The metal modified precursor synthesized was crosslinked with dicumylperoxide (DCP) as initiator for hydrosilylation and polymerization reaction. Subsequently pyrolysis of this material resulted in a ceramic yield of 61%, determined by thermogravimetric measurements.

Kraus et al. (2009) carried out the development of polymer derived ceramic composite coatings on steel substrate based on polysilazane precursor ABSE and cubic boron nitride (cBN) particles as a passive filler. ABSE was selected as ceramic precursor due to the high ceramic yield, facility of handling in air and effective protection of metals against corrosion and oxidation. The solid ABSE precursor was dissolved and the cBN particles were dispersed in a solution of Di-n-butylether and a dispersant separately and combined afterwards. The final coating thickness obtained could be adjusted between 13 and 17 µm. The addition of cBN particles resulted in a lower shrinkage when compared to unfilled ABSE based coatings. Test proved that the PDC coating has the ability to protect mild steel effectively from oxidation up to 700 °C.

3.3 HYBRID ORGANIC INORGANIC POLYMER

Synthesis of hybrid organic inorganic compounds has attracted a number of studies regarding to the preparation of new materials with improved characteristics. Hybrid materials are prepared through the combination of organic and inorganic compounds which turns this material into a great alternative to obtain new materials. Usually it is not possible to find all good characteristics in the same compound.

Sometimes it is necessary to combine one or more compounds or substances to combine those characteristics and form a unique material.

Organic compound usually present good flexibility and processability, whereas inorganic compounds have a good thermal and chemical stability. Hybrid materials are homogeneous due to a molecular dimension mixture of compounds (Saegusa, 1995).

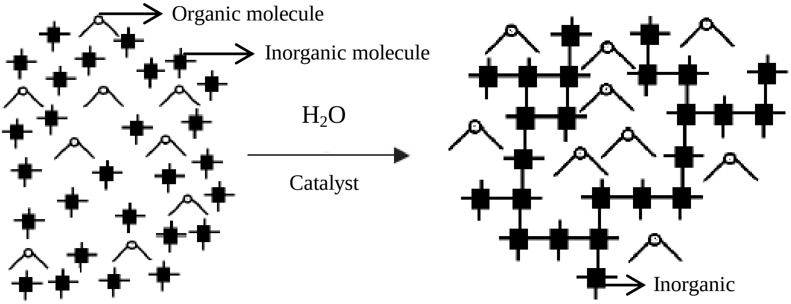
Generally hybrid materials can be prepared by three ways: physical incorporation of substances, through chemical bonds between compounds or by the combination of these two ways (José and Prado, 2005). One of the most important synthesis mechanisms is the sol-gel process. In sol-gel process, a metal alkoxide is used as the precursor of metal oxide, which is dispersed at molecular dimension by dissolution in an organic solvent such as alcohol. Then, sol-gel process for the conversion of metal alkoxide to metal oxide is performed in the presence of an organic polymer (Saegusa, 1995). It is also possible to form a heterogeneous material. This situation happen when the interaction between intermediate species of sol-gel reaction is not strong enough, resulting in a mixture of organic polymer and metal oxide.

3.3.1 Preparation of hybrid materials

As already mentioned it is possible to use different methods to prepare hybrid polymer compounds. According to José and Prado (2005) the resulting product can be classified in three major classes. Class 1 is formed by organic and inorganic compounds that interact through hydrogen bonding, Van der Waals forces or ionic bonds. The preparation of these compounds can occur by several synthetic routes, which are:

a) Via sol-gel process in which organic molecules randomly disperse in an inorganic network are trapped after the polycondensation of the inorganic precursor as presented in Figure 3.2 (Judeinstein and Sanchez, 1996).

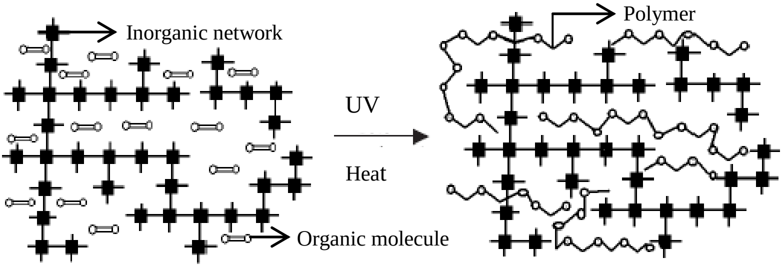
Figure 3.2 – Incorporation of organic molecules within an inorganic network prepared via sol-gel technique using inorganic molecules



Adapted (José and Prado, 2005)

b) Organic monomer dispersed in a pore inorganic matrix which are polymerized by UV radiation, heating or initiators as shown in Figure 3.3

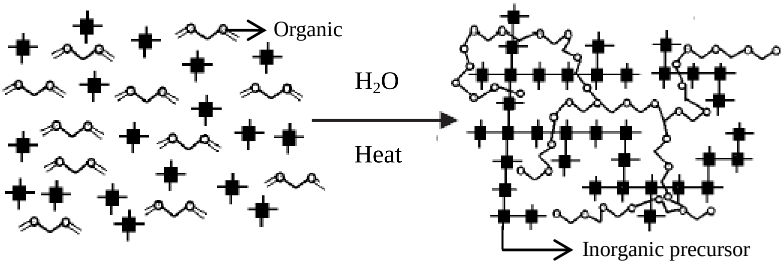
Figure 3.3 - Polymerization of organic monomers into an inorganic network generating polymer (adapted)



Adapted (José and Prado, 2005)

c) Formation of two simultaneous and independent networks from organic and inorganic precursors, previously functionalized, but without chemical bonding between the phases as shown in Figure 3.4

Figure 3.4 - Simultaneous formation of two networks from organic monomers and inorganic precursors



Adapted (José and Prado, 2005)

The Class 2 is formed of hybrid materials having organic and inorganic phases covalently or ionic-covalent by bonded. Class 3 would be a combination of the two previous classes.

Currently, studies of hybrid materials and the search for alternative materials boosted the preparation of organically modified silicon based materials. In the preparation route organic polymers have been incorporated to the silica network formed in situ, by the sol-gel process (Yamada et al., 1997). Komarneni et al. (1998) studied the use of organically modified silicate gels by using different alkyl groups to observe the effects of these groups on microporosity, hydrophobicity, pore volume and surface area.

3.4 SYNTHESIS TECHNIQUES

In this chapter some synthesis techniques used to prepare hybrid structures will be described.

3.4.1 Sol-gel process

By using the sol-gel technique a mostly oxide network can be generated by inorganic polymerization reactions using molecular precursors. These reactions used to take place in solution, in other words the synthesis of organic oxides in wet medium. The materials obtained present a high purity, homogeneity and low processing temperature. The chemistry of sol-gel process is based on the hydrolysis and condensation of molecular precursors (Minami, 2011).

The sol-gel process is the development of an inorganic networks through the formation of a colloidal suspension (sol) and the gelation of the sol to form a network in a continuous liquid phase (gel). The precursors for the synthesis of these colloids typically consist of a metal or non-metal atom surrounded by several reactive ligands. The raw material is processed to form a dispersed oxide and when in contact with water or dilute acid, forms the "sol", and the removal of this liquid produces the "gel", and the transition sol/gel controls the size and particle shape (Nunes, 2008).

The "sol" is composed by a colloidal particles suspension (size between 1 and 1000 nm) into a liquid, and the "gel" is formed by the rigid structure of colloidal particles (colloidal gel) or by polymer chains (polymer gel) which immobilize the liquid phase into interstices (Nunes, 2008) .

This technique is widely used due to the possibility of synthesizing inorganic non-metallic materials such as glass, ceramics or glass ceramic materials at low temperature compared to the conventional processes, which require high temperatures for melting glass and sintering ceramics (Colombo et al., 2010).

Malenovska et al. (2007) used sol-gel technique to prepare silica films on glass substrates with platinum, silver and gold nanoparticles homogeneously dispersed processed by mixing with tetraetoxysilanes {3-[(2- aminoethyl)amino]propyl} triethoxysilane complexes, followed by dip-coating and treatment with hydrogen at elevated temperatures.

Brusatin et al. (2011) used organic-inorganic hybrid materials based on 3-glycidoxypropyltrimethoxysilane in lithographic techniques radiation (UV, X- rays and electron beam) assisted or printing techniques, comparing them with products industrially available. The results allow to conclude that these new materials can be used for the desired purposes and strongly simplifies the conventional technique, reducing processing time and costs.

3.4.2 Emulsion polymerization

Emulsion polymerization is a widely used industrial process. One of the main advantages of this process is the possibility to achieve high molar mass polymers and high reaction rates. Furthermore, the low latex viscosity results in good heat dissipation and facilitates temperature control. By using water as a dispersing medium, the product also has advantages from an environmental and economic perspective on polymers that use polluting organic solvents and with high costs (Gilbert, 1995).

The main technique disadvantages is due to their multiphase nature and complexity of the mechanisms involved , which results in difficulty to modeling, monitoring and control. Many aspects of this reaction are interesting, e.g. the mechanisms of nucleation (Gilbert, 1995), dispersion of components between phases present in the system, the development of sensors to be used for in-line monitoring of this type of polymerization and the optimization and development of control strategies for this type of process (Chien and Penlidis, 1990; Esposito, 2010; Giudici, 2000; Vieira et al., 2002).

Oliveira (2003) studied the chemistry modification of natural rubber by grafting on polymer main chain of the hydrophobic substrate. Two monomers, methyl methacrylate (hydrophobic part) and dimethylaminethyl methacrylate (hydrophilic) were used. The results showed that grafting turns rubber more resistant to deformations as well as more hydrophilic, diversifying its use in industrial segments.

Lin et al. (2005) used this technique for synthesizing latex particles with core-shell morphology using polydimethylsiloxane (PDMS) as the core and poly(methylmethacrylate-co-butylacrylate) as the shell. The compatibility between the two polymer phases was changed by introducing vinyl groups into core latex. The presence of vinyl groups in the core caused the formation of cross-linking and promoted the seed deformation causing a strong impact on the final morphology. Other factors have also been studied, such as the increased hydrophobicity due to the incomplete shell formation.

Zou et al. (2007) synthesized organic-inorganic hybrid products by the polymerization with gamma rays where methyl methacrylate and butyl acrylate were polymerized. Ring opening of octamethyl cyclotetrasiloxane (D4) and tetramethyl-tetravinylcyclotetrasiloxane (VD4) were catalyzed with dodecylbenzenesulfonic acid to allow the polymerization of both. After this step, a second emulsion was made using the latex preformed as seed and feeding methacryloxy-propyl-trimethoxysilane (MATPMS). The latex obtained showed good storage stability, high mechanical stability and electrolytic resistance. Among other results, there is the reduction of water absorption with increasing amount of MATPMS on the composite.

3.4.3 Solution polymerization

Solution polymerization is a technique where the monomer is soluble in a non-reactive solvent. The heat exchange during the reaction is not as effective as in solution polymerization and used to influence in reaction rate, but applying solvent allows to work at higher temperatures than using water as continuous medium. Polysilazanes are also very sensitive to water, tuning solution polymerization an impossible choice. The major disadvantage of solution polymerization is the difficulty to remove the solvent after reaction and sometimes chain transfer reactions.

The solvent used in this process should be carefully chosen to avoid reactivity with monomer. Reactive solvent can result in undesired reactions and in some cases the autoacceleration effects. The autoacceleration of reaction can generate an excess of heat impossible to dissipate quickly enough, resulting in the increase of viscosity and loose of reaction control.

The temperature, concentration of initiator and the solvent /monomer volume fraction are factors that influence the solution polymerization, as they particularly affect the conversion and molecular weight of the final polymer. The type and amount of solvent influence the kinetic reaction and can cause chain transfer between the solvent and the polymerized chain (Augustinho, 2012). Using a high reaction temperature or a high concentration of initiator it is possible to obtain high conversions in short reaction times and also lower molecular weight (Ghosh et al., 1998). This behavior is attributed to the increase in the polymerization rate. Thus, the molecular weight of the polymer is significantly reduced because the initiator decomposition takes place more quickly. Furthermore, the gel effect is anticipated due to self-accelerating reaction (Jahanzad et al., 2005).

Ponnuswamy and Penlidis (1988) conducted solution polymerization reactions of methyl methacrylate to validate the mathematical model proposed by the authors. Different concentrations of initiator (0.05 mol.L^{-1} and 0.1 mol.L^{-1}) and reaction temperatures (65 °C, 70 °C and 75 °C) were analyzed to verify the influence on the conversion and molecular weight. The authors concluded that increasing the reaction temperature and keeping the other parameters constant, the conversion increases and the molecular weight decreases. This can be explained by the self-acceleration of radical initiator decomposition reaction resulting in the decrease of the molecular weight and increasing of conversion. The nonlinear model proposed by the researchers showed good agreement with experimental data, but for molar mass spectra was found a deviation attributed to experimental errors of Gel Permeation Chromatography (GPC).

Shin et al. (2011) synthesized via solution polymerization a composite silicon/poly(acrylonitrile-co-[3-trimethoxysilylpropylmethacrylate]) for use in lithium-ion battery of high performance, where the electromechanical properties were investigated. The incorporation of the organic polymer porous structure provided an efficient transport channel for the Li^+ ion during the formation of Si-Li alloy.

All techniques present advantages and disadvantages. In solution polymerization is possible to observe as advantage:
- Easy control of temperature and reaction medium;
- The polymer in solution is now ready for final application (but not in all applications).

On the other hand, it has disadvantages such as:
- The solvents cost are generally high;
- Toxicity of the solvent;
- Generally it is necessary to purify the final polymer reaction;
- Retardation of the reaction: the presence of the solvent may cause the delay of reaction and/or reduction of molecular weight due to chain transfer.

3.5 FREE RADICAL POLYMERIZATION KINETICS MECHANISM

The mechanism of a polymerization reaction is directly related to the interaction of each compound with each other and with the system. This interaction plays a key role in the evolution of the size and particle size distribution in polymerization. The viscosity during the polymerization and its variation with time is a result of conversion (Jahanzad et al., 2005), e.g. it is considered in the polymerization, to describe the particles size distribution in a realistic mathematical model the coalescence and breaking phenomena and its dependence on the chemical kinetics (Machado, 2000). As each drop of the monomer in polymerization is considered as a mini mass reaction it is assumed that the kinetic behavior is very similar to that of bulk polymerization. Many studies in the literature assume that hypothesis (Billmeyer, 1984; Mano, 1985; Biesenberger and Sebastian, 1983; Takamatasu et al., 1988; Kim and Choi, 1989; Dowding and Vincent, 2000). When this hypothesis is adopted this implies that the particle size, concentration and type of stabilizer should not influence the reaction kinetics in the case of homopolymerization. Making those considerations the reaction mechanism is composed by four basic stages: initiation, propagation, chain transfer and termination.

3.5.1 Initiation

Initiation step can occur by two different mechanisms, the decomposition of a thermal initiator or the thermal initiation of monomer. In the initiator decomposition, a free radical initiator reacts with the molecules of the monomer forming the primary polymer chain. Thermal monomer initiation reaction occurs when the temperature of thermal polymerization is attained. The most used initiators are peroxides and azo compounds. In addition, due to the large amounts of parallel reactions occurring in the reaction medium, not all free radicals from the initiator will initiate the formation of a polymer chain (Biesenberger and Sebastian, 1983; Odian, 1991).

The decomposition reaction of the initiator and the formation of the primary polymer chain are respectively in equations 3.8 and 3.9.

$$I \xrightarrow{K_d} 2R \cdot \tag{3.8}$$

$$R \cdot + M \xrightarrow{K_{iq}} P_1 \cdot \tag{3.9}$$

3.5.2 Propagation

In the propagation step is the stage where the growth of the polymer chain. The reaction occurs between the active primary polymer chains obtained at initiation with the monomer to form a new active intermediate chain, according to equation 3.10:

$$P_n \cdot + M \overset{K_p}{\rightarrow} P_{n+1} \cdot \tag{3.10}$$

With each reaction step a new monomer molecule is added to the radical formed in the previous step. The exchange reaction of the formed macromolecules will be different due to differences in the length. However, all rates converge to the same value of kp. This hypothesis is known as Long Chain Hypothesis (LCH) and admits that all chains exhibit the same reactivity regardless of the number of monomer units (Biesenberger and Sebastian, 1983; Odian, 1991).

3.5.3 Chain Transfer

A chain transfer reaction occurs when a growing polymer chain is transferred to another molecule, reducing the average molecular weight of the final polymer. This reaction can be introduced in a polymerization using a chain transfer agent or as a result from unavoidable side-reaction. Several chain transfers are possible and represented by equations 3.11 e 3.12.

To solvent $$P_n\cdot + S \xrightarrow{K_{trs}} D_n + R\cdot \tag{3.11}$$

To monomer $$P_n\cdot + M \xrightarrow{K_{trm}} D_n + P_1\cdot \tag{3.12}$$

3.5.4 Termination

This step is responsible for the termination of a growing molecule to form a stable product. The reactions can be terminated by combination, disproportionation and/or chain transfer to monomer. This work will be considered only termination by combination.

$$\mathrm{P_n}\cdot + \mathrm{P_m}\cdot \xrightarrow{\mathrm{K_{tc}}} \mathrm{D_{n+m}} \tag{3.13}$$

Where:
I : initiator molecule;
R· : active initiator radical;
M: monomer molecule;
$\mathrm{P_1}\cdot$, $\mathrm{P_n}\cdot$, $\mathrm{P_{n+1}}\cdot$, $\mathrm{P_n}\cdot$: active polymer chain with size 1, n, n+1 e m;
$\mathrm{D_{n+m}}$: Inactive polymeric chain with n+m;
$\mathrm{K_{d,}}\ \mathrm{K_{iq,}}\mathrm{K_{p,}}\mathrm{K_{tc}}$: Kinetic reaction constants.

3.6 PHENOMENA THAT AFFECT THE FREE RADICAL POLYMERIZATION REACTIONS

3.6.1 Gel Effect

The gel effect is a reduction in the rate of termination of active chains due to a decrease in the mobility of radicals. This reduction results in increased polymerization rate further increasing the viscosity of the reaction locus. This effect is also described in the literature as

Tromsdorff Effect or Norrish-Smith (Chiu et al, 1983; Biesenberger and Sebastian, 1983; Odian, 1991).

Some final reaction parameters can be affected by the gel effect as the polymer molar mass. The gel effect can result in the formation of nonlinear chains, which are very significant when is desired to follow a model of free radical polymerization (Kiparissides, 1996). It is observed gel effect in the reaction medium when, e.g. it is detected an increase in viscosity and hence a decrease in the heat transfer coefficient between the fluid and the reactor (Crowley and Choi, 1996). A decrease in the heat transfer coefficient can promote an uncontrolled reaction temperature resulting in undesired products.

3.6.2 Cage Effect

The cage effect is directly related to the efficiency of the initiator. Comparing the amount of initiator that decomposes during the reaction to that effectively initiates polymer chains, it is observed that not all the released radicals capable of reacting will initiate the formation of a chain. This occurs due to the existence of side reactions in the system, even prior to formation of the polymer chain.

It is normal to associate the decomposition reaction of the initiator to an efficiency factor f, which can vary over the course of the reaction (Biesenberger and Sebastian, 1983).

In chemical initiation, the initiator decomposes into two or more active radicals. These radicals diffuses before get stuck in a sort of cage, formed by polymer molecules involving them. Inside the cage, the primary radicals can recombine to form the primary initiator molecule or decompose into secondary radicals and react with each other forming stable species unable to initiate a new polymer chain again. Inside the cage, the primary radicals can react with the monomer molecules or simply diffuse out of the cage. Once out of the cage, the radicals can react with monomer molecules, starting a new polymer chain react with secondary radicals, disabling both, or react with a primary radical, also disabling both.

After diffused out of the cage, the probability of starting a new radical polymer chain is much greater because the amount of monomer molecules against any species is greater. If the concentration of monomer in the system is low, the efficiency factor is also low. Increasing the concentration of monomer, the efficiency factor increases according a constant value less than 1.0. The efficiency factor also depends on the concentration of the solvent medium, because there is competition between solvent and monomer molecules to react with the radical formed (Biesenberger and Sebastian, 1983; Odian, 1991).

3.6.3 Glass Effect

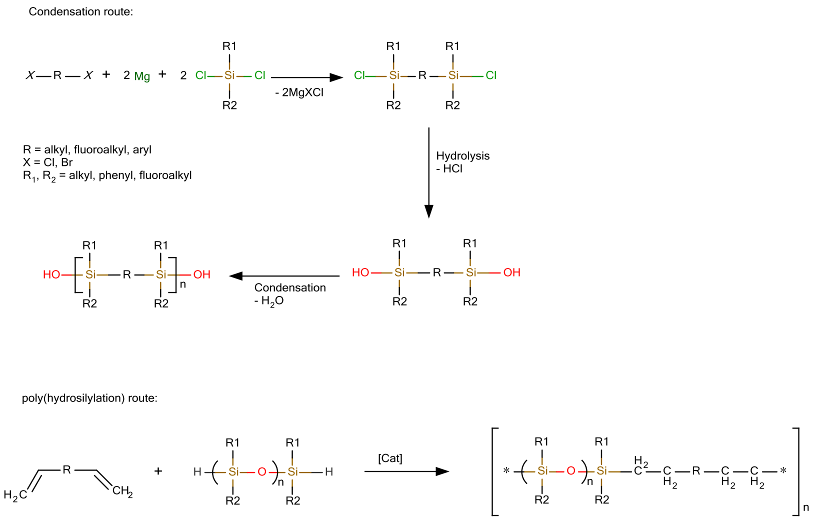
The glass effect is considerable in polymerizations where the reaction temperature is below the glass transition temperature of the polymer (Tg). The consequence of this phenomenon is the "freezing" of the reaction medium. With the increasing of conversion, there is an increase in the glass transition temperature of polymer/monomer blend and depending on the system may be a critical conversion in which the Tg becomes equal to the polymerization temperature (Kiparissides, 1996). Thus, the propagation rate drops drastically due to the entanglement of polymer matrix chains ceasing mobility polymeric radicals and monomer molecules.

The still active chains will terminate by reaction diffusion, also called residual termination, where the centers of radical move only by the addition of monomer molecules via propagation (Marten and Hamielec, 1982; Huang and Lee, 1989; Tefera et al., 1997, Ghosh et al., 1998).

3.7 HYDROSILYLATION PROCESS

Hydrosilylation reactions represent an efficient methodology to perform a catalytic addition of Si-H bonds to a carbon-carbon or carbon-heteroatom double bonds (Sorarù et al., 2012). Other types of catalysts may be nucleophiles, Lewis acids, supported metals, metals reduced *in situ* or transition metal complexes attached to inorganic or polymeric support (Putzien et al., 2010). A range of new ligand classes like diimines or carbenes have been tested as ligands of the catalyst, several lanthanides presented a good efficiency as catalysts, many different conditions have been used to improve reactions and efficiency. Hydrosilylation has become an important tool in chiral synthesis promoting new materials from block copolymers to dendrimers and functionalized silicones (Putzien et al., 2010).

Hydrosilylation is an important strategy for the development of new materials combining chemical properties of silicon-based materials and organic compounds. These organo-silicones can be prepared mainly via two routes: the condensation of silanol compounds or the polyhydrosilylation of olefins or dienes with (di)hydride- or oligosiloxanes, according to Scheme 3.1 (Guida-Pietrasanta et al., 2005).



Scheme 3.1 (Guida-Pietrasanta et al., 2005)

To promote this type of reaction exist a great variety of catalysts. The most used catalysts are hexachloroplatinic acid $H_2(PtCl_6)$ (Speier's catalyst) and $[Pt_2(\text{sym-tetramethyldivinyldisiloxane})_3]$ (Karstedt's catalyst).

Skoda-Földes et al. (1991) performed hydrosilylation of C=C bonds in the presence of transition metal $PtCl_2(PhCN)_2$, $RhCl(PPh_3)_3$ and platinum phosphine catalysts. A range of different products was formed. The product distribution is totally dependent on the silane type and catalyst for each vinyl compound used. Also the inactivity of platinum(II)-phosphine complexes in the absence of air was observed. However some platinum(0)-phosphine catalysts are effective under argon for the hydrosilylation of methyl methacrylate.

Tsumura and Iwahara (1999) developed crosslinked polycarbosilanes using hydrosilylation techniques. Different monomers were solved in tetrahydrofuran, mixed with a dimethyl maleate solution and Pt catalyst. Samples were placed in an oven during 16h (50 °C) and submitted to a thermal treatment. Authors concluded that it is necessary to form a network with high chain density and rigid-rod units to obtain high mechanical strength of crosslinked polycarbosilanes.

Grunlan et al. (2003) prepared copoly(carbosiloxane) with pendant 3,3,3-trifluoropropyl groups using Pt catalyst with the intention to achieve the useful properties of both siloxane and fluoro polymer systems. Generally siloxanes present lower values of glass transition because large bond angles and bond lengths, in this case associated with the dimethylsiloxane backbone, producing a great conformational flexibility. For almost all copolymers was observed an increase of glass transition temperatures due to adjacent CF_3 groups. Thermogravimetric analyses showed the stability of copolymers until 380 °C (N_2 atmosphere).

Sorarù et al. (2012) executed hydrosilylation between a polysiloxane and polycarbosilane aerogels using a Pt catalyst. It has been most used to cross link siloxanes and form preceramic networks (Blum et al., 2005). Nyczyk et al. (2012) also relate the possibility of the use of hydrosilylation to crosslink linear polysiloxanes with regular vinyl groups distributed along the chain. To catalyze this reaction was used Karstedt catalyst.

4. EXPERIMENTAL METHODOLOGY AND MATERIALS

Experimental part was executed in cooperation between Lehrstuhl Keramische Werkstoffe – Germany and Laboratório de Controle de Processos – Brazil. This part was divided in two systems according to each reaction methodology, presented below. Systems are detailed according Figure 4.1.

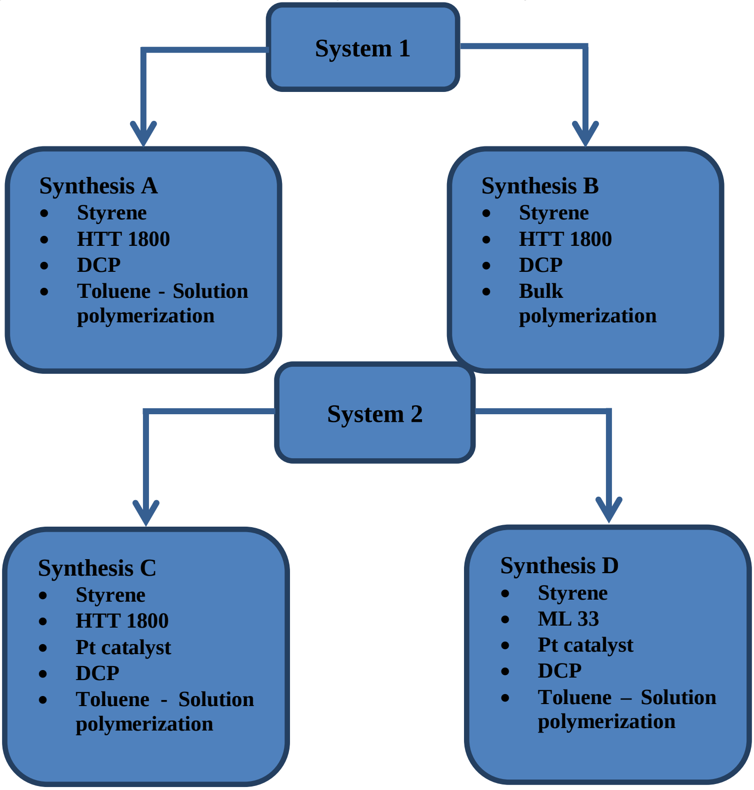
System 1

- Synthesis of an organic-inorganic polymer using free radical bulk polymerization (synthesis A);
- Synthesis of an organic-inorganic polymer using free radical solution polymerization (synthesis B);
- Characterization using Fourier Transformed Infrared (FTIR), Thermogravimetric analysis with Fourier Transformed Infrared (TGA-FTIR), Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC).

System 2

- Synthesis of an organic-inorganic polymer using metallic catalyst, free radical initiator by solution polymerization (synthesis C and D);
- Characterization using crosslinking content, Fourier Transformed Infrared (FTIR), Thermogravimetric analysis with Fourier Transformed Infrared (TGA-FTIR), Thermogravimetric analysis (TGA), Differential Scanning Calorimetry (DSC), Nuclear Magnetic Resonance (NMR).

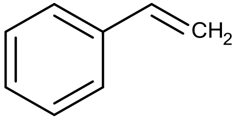
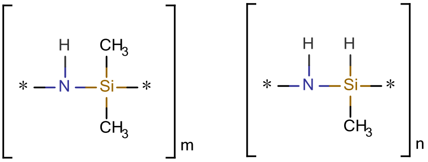
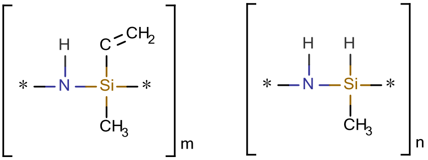
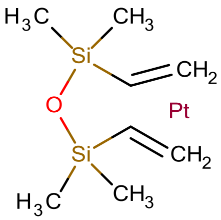
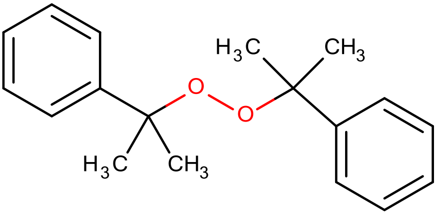
Figure 4.1 – Detailed flowchart of synthesis reaction systems.



4.1 REAGENTS

Styrene and Dicumyl peroxide were purchased from Sigma Aldrich. HTT 1800 and ML33 were gently provided by Clariant. Toluene was provided by Sigma-Aldrich. Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene 2% was purchased at ABCR GmbH & Co. All reagents were used without further purification. Table 4.1 displays the possible to observe molecular structures and properties from reagents.

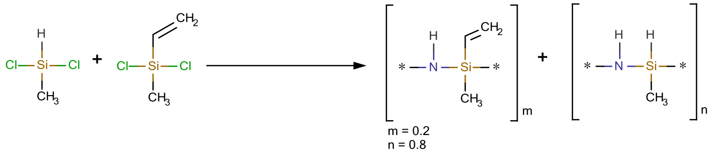
Table 4.1 - Molecular structures and properties from reagents.

Compound	**Type**	**Structural formula**
Styrene	Monomer	
ML33	Precursor	 m = 0.33 n = 0.67
HTT1800	Precursor	 m = 0.2 n = 0.8
Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyl disiloxane	Catalyst	
Dicumyl peroxide	Initiator	

4.2 CHARACTERIZATION OF PRECURSORS

4.2.1 Precursor HTT 1800

HTT 1800 is the product obtained from coammonolysis synthesis between dichloromethylvinylsilane and dichloromethylsilane. In Equation 4.1 the coammonolysis of dichloromethylvinylsilane and dichloromethylsilane (simplified structures of product), where m=0.2 and n=0.8 is represented.



(4.1)

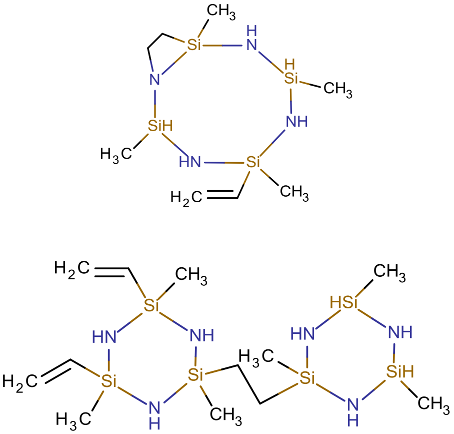
The product obtained is liquid and colorless. Traβl (2001) executed NMR characterization of the same structure units contained in HTT 1800, which is presented in Table 4.2.

Table 4.2 - NMR characterization to HTT 1800 (Traßl, 2001).

Nucleus	δ(ppm)	Chemical structure
^{1}H	-0.15 — 0.60	$\mathrm{Si{-}}\mathbf{CH_3}$
	0.60 — 1.20	$\mathrm{Si{-}N}\mathbf{H}\mathrm{{-}Si}$
	4.70 — 5.25	$\mathrm{Si{-}}\mathbf{H}$
	5.70 — 6.0	$\mathrm{Si{-}CH{=}}\mathbf{CH_2}$
	6.0 — 6.30	$\mathrm{Si{-}C}\mathbf{H}\mathrm{{=}CH_2}$
^{13}C	1.0 — 6.0	$\mathrm{Si{-}}\mathbf{C}\mathrm{H_3}$
	8.0 — 16.0	$\mathrm{Si{-}}\mathbf{C}\mathrm{H_2{-}}\mathbf{C}\mathrm{H_2{-}Si}$
	131	$\mathrm{Si{-}}\mathbf{C}\mathrm{H{=}CH_2}$
	142	$\mathrm{Si{-}CH{=}}\mathbf{C}\mathrm{H_2}$
^{29}Si	-14.8	$\mathbf{Si}\mathrm{(CH_3)(CH{=}CH_2)}$
	-17 — -24	$\mathbf{Si}\mathrm{H(CH_3)}$

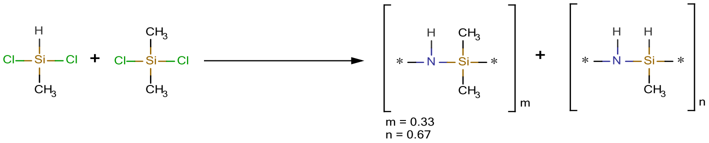
The presence of multiple signals broad and sharp lines and the respective values of the chemical shifts in the spectrum indicate that the precursor is mainly composed of a mix of six and eight-membered rings with different units. In Figure 4.2 are presented two possible structures of the HTT 1800 precursor.

Figure 4.2 - Two possible structures of the HTT 1800 precursor.



4.2.2 Precursor ML33

ML33 is the product obtained from coammonolysis synthesis between dichlorodimethylsilane and dichloromethylsilane. In Equation 4.2 is displayed the coammonolysis of dichlorodimethylnilsilane and dichloromethylsilane (simplified structures of product), where m=0.33 and n=0.67.



(4.2)

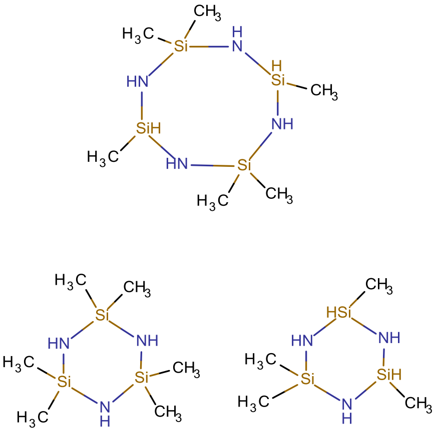
The product obtained is liquid and colorless. NMR characterization of ML33 is presented in Table 4.3.

Table 4.3 - NMR characterization of ML33 (Based on results founded to HTT 1800 by Traßl, 2001).

Nucleus	δ(ppm)	Chemical structure
^{1}H	-0.15 — 0.60	Si–C$\mathbf{H_3}$
	0.60 — 1.20	Si–N**H**–Si
	4.70 — 5.25	Si–**H**
^{13}C	1.0 — 6.0	Si–**C**H$_3$
	8.0 — 16.0	Si–**C**H$_2$–**C**H$_2$–Si
^{29}Si	-17 — -24	**Si**H(CH$_3$)

Figure 4.3 presents two possible structures formed of ML 33 precursor.

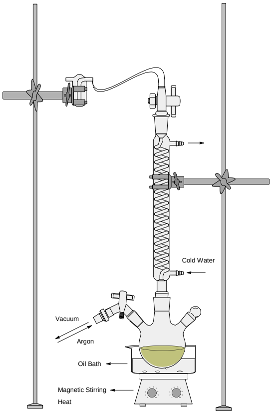
Figure 4.3 - Two possible structures formed by ML 33.



4.3 SYNTHESIS OF ORGANIC-INORGANIC POLYMER

Reactions were performed at Lehrstuhl Keramische Werkstoffe using reagents described above. Figure 4.4 presents the equipment used for all reactions.

Figure 4.4 - Reaction system used for bulk polymerization and solution polymerization.



4.3.1 Synthesis of an organic-inorganic polymer with dicumyl peroxide by free radical bulk polymerization (System 1 – Synthesis A)

HTT 1800 was used as inorganic oligomer. Styrene was used as organic monomer. The reaction was performed using a 3-neck flask equipped with mechanical stirrer, a reflux condenser, an inlet for feeding reagents, an inlet for Argon and an oil bath with control temperature system as presented in Figure 4.3. The glass flask was charged with organic monomer styrene 60 wt.% (6 g) and dicumyl peroxide 3 wt.% (0.3 g) at room temperature. The reactor was heated up to 90 °C and the inorganic compound HTT 1800 40 wt.% (4 g) was added drop wise and mixed under higher magnetic stirring. After all compounds were mixed the temperature was increased to 135 °C for about 5 hours. All procedures were executed under Argon atmosphere. Polymer was removed from the flask and pulverized using liquid nitrogen.

4.3.2 Synthesis of an organic-inorganic polymer with dicumyl Peroxide by free radical solution polymerization (System 1 – Synthesis B)

HTT 1800 was used as inorganic oligomer. Styrene was used as organic monomer. The reaction was performed using a 3-neck flask equipped with mechanical stirrer, a reflux condenser, an inlet for feeding reagents, an inlet for Argon and an oil bath with control temperature system as presented in Figure 4.3. The glass flask was charged with organic solvent toluene (17 mL), organic monomer styrene 60 wt.% (6 g) and dicumyl peroxide 3 wt.%/wt.% styrene (0.18 g) at room temperature. At this point toluene was added as a solvent. The reactor was heated up to 90 °C and the inorganic compound HTT 1800 40 wt.% (4 g) was added drop wise and mixed under higher magnetic stirring. After all compounds were mixed the temperature was increased to 135 °C for about 5 hours. All procedures were executed under Argon atmosphere. The product obtained was dried in vacuum for 3 hours. Polymer was removed from the flask and pulverized using liquid nitrogen.

Additionally, reactions were executed using different ratios of Styrene/HTT 1800 to analyze the thermal behavior of the hybrid polymers. The ratios chosen to this study were:

- Styrene 80 wt.%/HTT 1800 20 wt.%/DCP 3 wt.%

- Styrene 70 wt.%/HTT 1800 30 wt.%/DCP 3 wt.%
- Styrene 60 wt.%/HTT 1800 40 wt.%/DCP 3 wt.%
- Styrene 56 wt.%/HTT 1800 44 wt.%/DCP 3 wt.%

Due to the result similarities of pure organic and inorganic polymers obtained by bulk and solution polymerization it will be presented, when comparing both techniques (Synthesis A and B), the TGA, FTIR and DSC curves obtained by bulk polymerization.

4.3.3 Synthesis of an organic-inorganic polymer using metallic catalyst and dicumyl peroxide by solution polymerization (System 2 – Synthesis C)

HTT 1800 was used as inorganic oligomer. Styrene was used as organic monomer. The reaction was performed using a 3-neck flask equipped with mechanical stirrer, a reflux condenser, an inlet for feeding reagents, an inlet for Argon and an oil bath with control temperature system. The glass flask was charged with organic monomer styrene 60 wt.% (0.0570 mols) and Pt catalyst 0.2 wt.% at room temperature. The reactor was heated up to 70 °C and the inorganic compound, HTT 1800 40 wt.% (0.0124 mol) was added, mixed under higher magnetic stirring and allowed to react during 5 hours. Then DCP 3 wt.% was added and the temperature was increased to 135 °C for about 1 hours. All procedures were executed under Argon atmosphere. Product was removed from the flask and pulverized using liquid nitrogen.

4.3.4 Synthesis of an organic-inorganic polymer using metallic catalyst and dicumyl peroxide by solution polymerization (System 2 – Synthesis D)

ML33 was used as inorganic oligomer. Styrene was used as organic monomer. The reaction was performed using a 3-neck flask equipped with mechanical stirrer, a reflux condenser, an inlet for feeding reagents, an inlet for Argon and an oil bath with control temperature system. The glass flask was charged with organic monomer Styrene 60 wt.% (0.0576 mols) and Pt catalyst 0.2 wt.% at room temperature. The reactor was heated up to 70 °C and the inorganic compound ML 33 40 wt.% (0.0209 mols) was added, mixed under higher magnetic stirring and allowed to react during 5 hours. Then DCP 3 wt.% was added and the temperature was increased to 135 °C for about 1 hours. All procedures were executed under Argon atmosphere. Product was removed from the flask and pulverized using liquid nitrogen.

4.4 CHARACTERIZATION METHODS

4.4.1 Fourier Transformed Infrared (FTIR)

FTIR analysis was performed to estimate functional groups of polymers obtained and as a possible tool to predict structural units. Samples were pulverized using liquid nitrogen under argon atmosphere. No special sample preparation was necessary due to the use of diamond ATR. The spectra were measured with a Bruker spectrometer with ATR diamond unit at Lehrstuhl Keramische Werktoffe.

4.4.2 Thermogravimetric analysis with Fourier Transformed Infrared (TGA-FTIR)

TGA-FTIR was executed to observe which gaseous products were released during thermal treatment, crosslinking and pyrolysis of samples. The equipment used was a TG/DTA from Netzsch (STA 409) in argon atmosphere until 1000 °C located at Lehrstuhl Keramische Werktoffe. Samples were previously pulverized with liquid nitrogen under argon atmosphere. An alumina crucible was used. Heat rate was 10 K min^{-1}. During TGA analysis, gaseous products started to be liberated in a heated gas line. Liquid nitrogen was used cooling detector from FTIR spectrometer Bruker (VECTOR 22) and avoids injuries to measuring cells where absorption spectrum was detected. It was possible to follow which gaseous species were formed during analysis.

4.4.3 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry analysis (DSC) was performed at Lehrstuhl Polymer Werkstoffe – Universität Bayreuth using a differential scanning calorimetry equipment from TA Instruments model Q1000. Samples (5-20 mg) for DSC analysis were heated at 10 °C.min^{-1} to 300 °C under Argon atmosphere. DSC analysis was used to monitor heat effects associated with transitions and chemical reaction as a function of temperature.

4.4.4 Determination of gel content

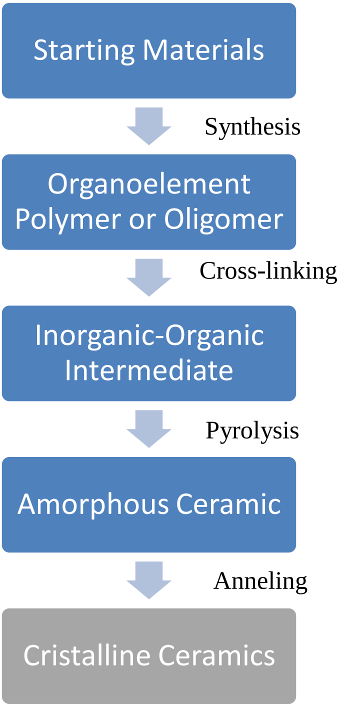
The gel content corresponds to the insoluble fraction of crosslinked silazane (the crosslinked fraction of the sample). The gel content was determined after a toluene extraction using a simple vacuum extractor. About 0.5 g of sample was solubilized in 20 mL of toluene with magnetic stirring and heating up to 70°C. Samples were introduced in a cellulose thimble and extracted with toluene for 4 h. Insoluble fraction obtained after 4 h was then dried in an oven until a constant mass is obtained. The gel content can be calculated using Equation 4.3:

$$Gel\ content\ (\%) = \frac{Sample\ weight\ after\ drying}{Initial\ sample\ weight} \times 100 \quad (4.3)$$

4.4.5 Residual Mass Analysis (Tubular Oven)

Samples were treated in a tubular oven HERAEUS model RO 10/100 to execute the polymer-to-ceramic transformation. This process can be divided in a complex stages sequence of chemical and physical changes. Initially a synthesis is performed with starting materials, in this case organic monomer and inorganic oligomer. After synthesis a hybrid polymer was obtained with a certain crosslinking degree. The hybrid material was placed in a tubular oven and submitted to a thermal treatment, resulting initially in a higher crosslinked structure and subsequently in amorphous ceramic (after pyrolysis step).

Figure 4.5 - Flow chart representing the processing of silicon nitride/silicon carbide based ceramics (Kroke et al., 2000).



4.4.7 Nuclear Magnetic Resonance (NMR)

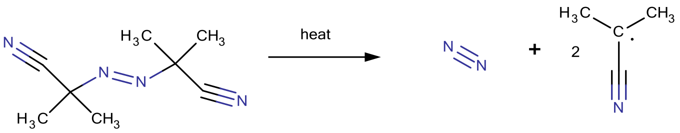
To investigate the chemical structure of products solid state ^{13}C and ^{29}Si solid NMR spectroscopy was used. This technique was preferred instead normal liquid NMR due to the high level of gel content and low solubility of samples. Analyses were executed at Federal University of São Carlos – UFSCar by Professor Dr. Antonio Gilberto. The equipment used was a Bruker solid state NMR model AVANCE III 14.1 Tesla.

5. RESULTS AND DISCUSSION

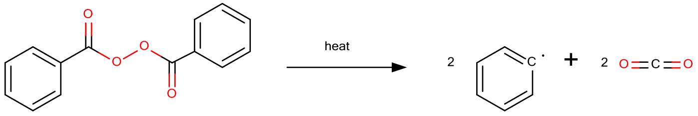
This chapter will be divided in two main parts according each synthesis system.

5.1 SYNTHESIS OF AN ORGANIC-INORGANIC POLYMER WITH DICUMYL PEROXIDE BY BULK AND SOLUTION POLYMERIZATION (SYSTEM A AND B)

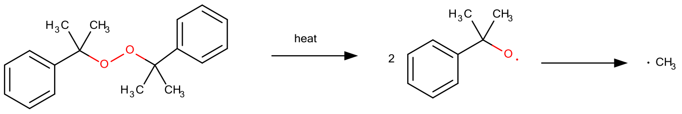
Styrene monomer was reacted with inorganic precursor and dicumyl Peroxide intending to execute a free radical polymerization with and without solvent, because reactive vinyl groups are available in both molecules. An initial test with different initiators, azobis(isobutyronitrile) (AIBN), benzoyl peroxide (BPO) and dicumyl peroxide (DCP) was performed to compare the preferential reactivity of inorganic precursor with the dicumyl peroxide, already observed by Toreki et al. (1990). It is known that DCP is not the best option as radical initiator for the organic monomer, although during initial tests showed that styrene reacts faster than the inorganic part. Toreki et al. (1990) presumed that dicumyl peroxides effectiveness is due to the formation of a methyl radical. Once HTT 1800 is presented as a six membered ring configuration (cyclic vinylsilazane) with trifunctionality, the gel point is reached at a very low degree of conversion (Toreki et al., 1990). A significant degree of conversion can be just observed applying a small radical as initiator. Equations 5.1, 5.2 and 5.3 show which radical is formed after initiation of AIBN, BPO and DCP, respectively.



(5.1)



(5.2)



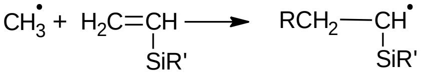
(5.3)

The reaction mechanism expected was a free radical polymerization, with DCP radicals attacking vinyl groups of organic and inorganic monomers. Reactivity for organic monomers can be easily founded in polymer handbooks, however for inorganic monomers is not so common. Different of styrene polymerization, where a linear polymeric structure is formed, inorganic oligomers containing vinyl groups intend to crosslinking. The characteristic of crosslinking product depends on type and concentration on peroxide, reaction temperature and time of curing (Hartung et al., 1962). Vinyl groups attached to silicon are reactive below 100 °C. According to Hartung et al. (1962) polymerization is best carried out in a temperature range of 110 °C to 150 °C. In this range of temperature, for inorganic monomer DCP was the best option with a half-life of 1 hour at 135 °C. Though, this reaction temperature was critical for styrene making impossible to separate thermal from radical initiation. The reaction mechanism expected between inorganic precursor HTT 1800 and dicumyl peroxide or styrene and dicumyl peroxide is presented in Equations 5.4 – 5.11.

Initiator decomposition

$$R'COOCR' \xrightarrow[-CO_2]{} CH_3^{\bullet} \qquad (5.4)$$

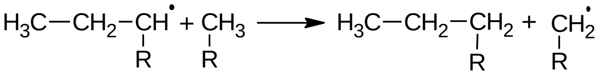
Initiation



$$CH_3^{\bullet} + H_2C{=}\underset{SiR'}{CH} \longrightarrow RCH_2{-}\underset{SiR'}{CH^{\bullet}}$$

(5.5)

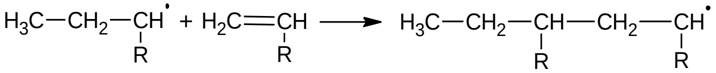
Chain Transfer



$$H_3C{-}CH_2{-}\underset{R}{CH^{\bullet}} + \underset{R}{CH_3} \longrightarrow H_3C{-}CH_2{-}\underset{R}{CH_2} + \underset{R}{CH_2^{\bullet}}$$

(5.6)

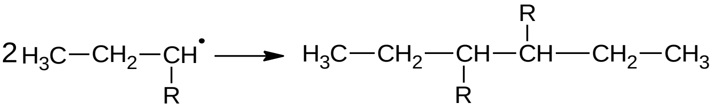
Propagation



$$H_3C{-}CH_2{-}\underset{R}{CH^{\bullet}} + H_2C{=}\underset{R}{CH} \longrightarrow H_3C{-}CH_2{-}\underset{R}{CH}{-}CH_2{-}\underset{R}{CH^{\bullet}}$$

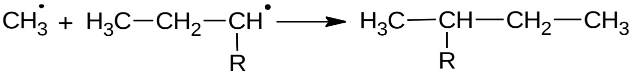
(5.7)

Termination



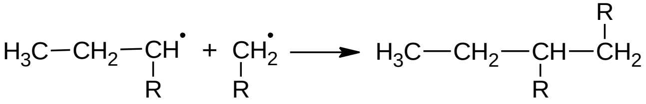
$$2\,H_3C{-}CH_2{-}\underset{R}{CH^{\bullet}} \longrightarrow H_3C{-}CH_2{-}\underset{R}{CH}{-}\overset{R}{CH}{-}CH_2{-}CH_3$$

(5.8)

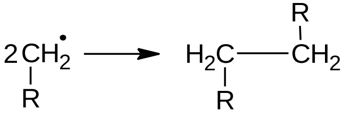


$$CH_3^{\bullet} + H_3C{-}CH_2{-}\underset{R}{CH^{\bullet}} \longrightarrow H_3C{-}\underset{R}{CH}{-}CH_2{-}CH_3$$

(5.9)



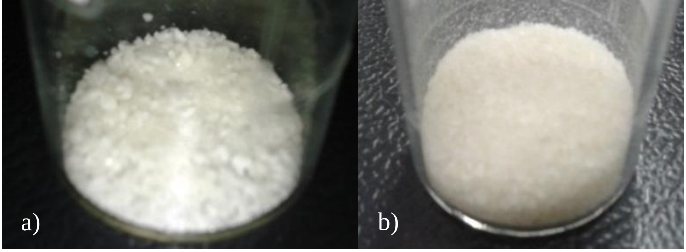
$$H_3C{-}CH_2{-}\underset{R}{\underset{|}{CH^{\bullet}}} + \underset{R}{\underset{|}{CH_2^{\bullet}}} \longrightarrow H_3C{-}CH_2{-}\underset{R}{\underset{|}{CH}}{-}\overset{R}{\overset{|}{CH_2}} \quad (5.10)$$



$$2\underset{R}{\underset{|}{CH_2^{\bullet}}} \longrightarrow H_2\underset{R}{\underset{|}{C}}{-}\overset{R}{\overset{|}{CH_2}} \quad (5.11)$$

After synthesis two products were obtained, styrene/HTT 1800 (bulk polymerization) and styrene/HTT 1800 (solution polymerization). Both polymers (Figure 5.1) were yellow, brittle and solid products. The solubility of these products was investigated using toluene, cumene, THF, methanol, acetone and ethanol as solvents.

Figure 5.1 – Hybrid polymer (a) styrene 60 wt.% /HTT 1800 40 wt.%/DCP 3 wt.% and (b) styrene 60 wt.% /HTT 1800 40 wt.% DCP 3 wt.% obtained by bulk and solvent polymerization, respectively.



5.1.1 Thermogravimetric analysis (TGA)

Thermogravimetic analysis was performed to investigate the thermal degradation mechanism, to determine the ceramic yield and to characterize differences because of the different reaction approaches. Therefore also samples of the pure precursor and polystyrene as well as samples of hybrid composition were analyzed (Figure 5.2, and in details showed in Figure 5.3).

Figure 5.2 – Thermogravimetric analysis of HTT 1800/DCP 3 wt.%, styrene/DCP 3 wt.%, styrene 60 wt.% /HTT 1800 40 wt.% DCP 3 wt.% bulk polymerization and styrene 60 wt.%/ HTT 1800 40 wt.%/DCP 3 wt.% solvent polymerization.

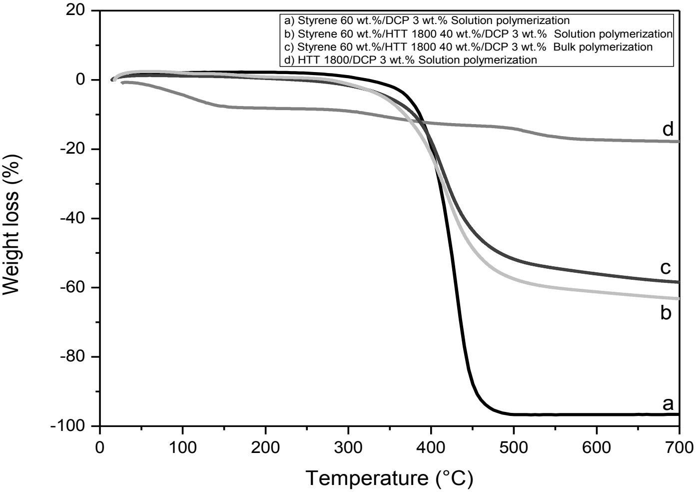
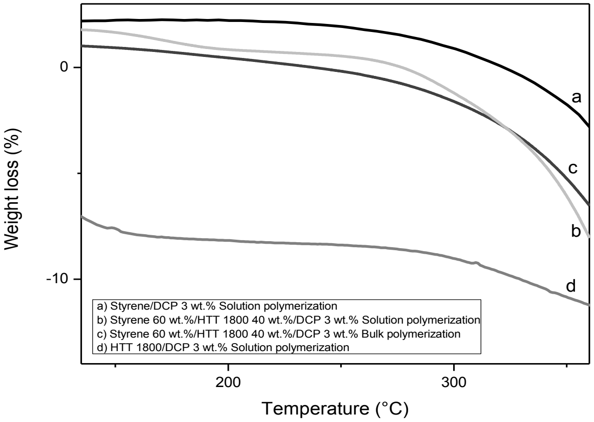


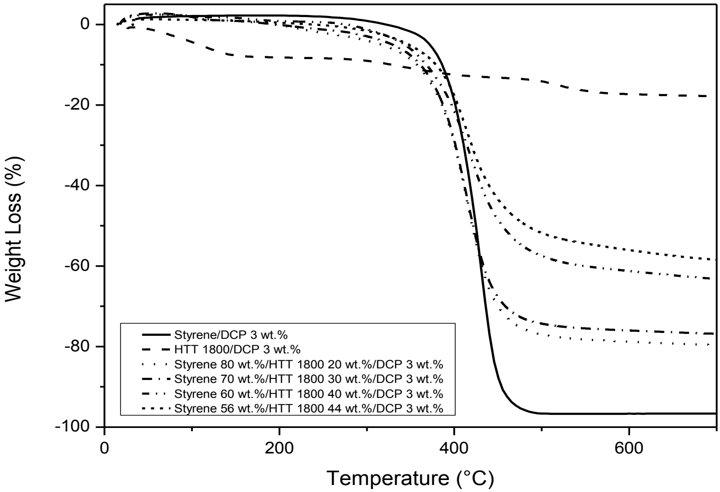
Figure 5.3 – Magnification of figure 5.2.



A decrease of weight loss was detected when polystyrene (Figure 5.2, line a) is compared to hybrid compounds obtained from the reaction between polystyrene and HTT 1800 (Figure 5.2, line b and c). PS/HTT

1800 bulk polymerization (Figure 5.2, line c) weight loss was 57 % and PS/HTT 1800 solution weight loss was 62 % (Figure 5.2, line b). Pure polystyrene (Figure 5.2, line a) presented 100% weight loss. It was expected to obtain a reduction of this weight loss combining polystyrene with HTT 1800, which has an excellent ceramic yield in comparison to polystyrene. The weight loss obtained for the PS 60 wt.%/HTT 1800 wt.% polymer composition was better than expected, hence the hybrid material should presents a theoretical weight loss of 68 % (60 % of Polystyrene and 8% of HTT 1800). Another important point is the temperature when the polymer or the hybrid polymer starts to decompose. For pure polystyrene and PS/HTT 1800 obtained by bulk polymerization, the initial decomposition temperature was around 400 °C. Although in PS/HTT 1800 obtained by solution polymerization was detected an initial decomposition at 200 °C due to the presence of solvent and consequently chain transfer reactions. Solvent act as chain transfer agent resulting in low mass oligomers instead copolymerization. A study with different concentrations of HTT 1800 in the hybrid composition was performed. Results are shown in Figure 5.4.

Figure 5.4 - Thermogravimetric analysis of HTT 1800/DCP 3 wt.%, styrene/DCP 3 wt.%, styrene/HTT 1800/DCP 3 wt.% with different styrene/HTT 1800 ratios reacted by solution polymerization.



As expected with increase in the amount of HTT 1800, a decrease of the measured weight loss was observed. No difference between curves related to degradation mechanism was determined. Table 5.1 shows a comparative between theoretical and measured weight loss.

Table 5.1. Comparison between measured and theoretical weight loss from samples with different styrene/HTT 1800 ratioa synthesized by solution polymerization method.

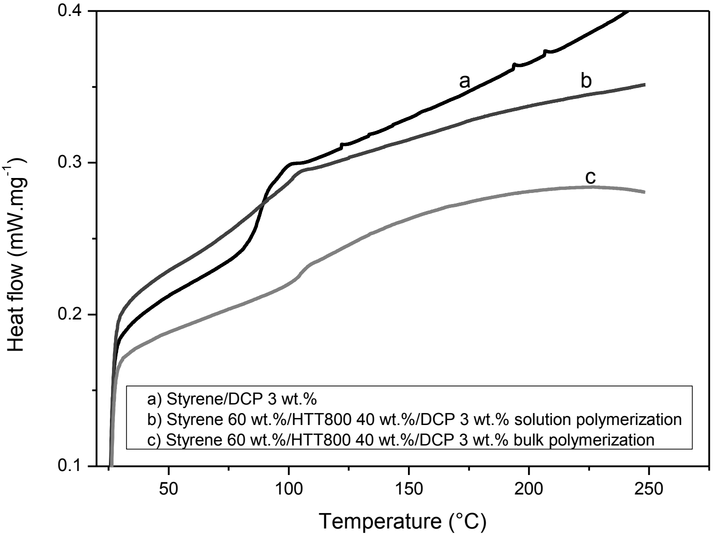
Sample	**Theoretical Weight loss (%)**	**Measured weight loss (%)**
Styrene 80 wt.%/HTT 1800 20 wt.%/DCP 3 wt.%	84	79
Styrene 70 wt.%/HTT 1800 30 wt.%/DCP 3 wt.%	76	76
Styrene 60 wt.%/HTT 1800 40 wt.%/DCP 3 wt.%	68	61
Styrene 56 wt.%/HTT 1800 44 wt.%/DCP 3 wt.%	64	58

As can be seen in table 5.1 a slight reduction of the measured weight loss in comparison to the theoretical values is presented. This reduction represents evidence that a part of styrene reacted with HTT 1800 resulting in a hybrid structure. These results are in good agreement with the objective of the work to include the carbon of styrene partially in the resulting ceramic material. The results are an evidence for a successful combination of HTT 1800 with styrene leading to a hybrid materials. The obtained results have a high potential to reduce the cost of final ceramic products, to modify chemical properties or even to produce new types of SiCN/C materials.

5.1.2 Differential Scanning Calorimetry (DSC)

To investigate glass transition temperature (Tg) Differential Scanning Analysis (DSC) was executed for pure polymer samples and hybrid compositions made by bulk and solution polymerization. The curves of second heating were chosen to characterize Tg of the hybrid polymers due to the influence that heating has on polysilazanes glass transition behavior. DSC curves are shown in Figure 5.5.

Figure 5.5 - Differential Scanning Calorimetry of Styrene/DCP 3 wt.%, Styrene 60 wt.%/HTT 1800 40 wt.%/DCP 3 wt.% bulk and Styrene 60 wt.%/HTT 1800 40 wt.%/DCP 3 wt.% solution polymerization.



DSC analysis is an excellent tool to analyze organic polymers presenting well defined signals of glass transition and melting transitions. However polysilazanes DSC curves are not well defined (weak Tg shifts) related to the complex structure of these compounds. Also the higher the molecular weight and polydispersity of the polymer the higher is the degree of crosslinking of the polymer and the shift upward in the DSC tends to disappear (Flores et al., 2013). Figure 5.5 shows a strong Tg shift to polystyrene and weaker shifts for both PS/HTT 1800 products. Only one shift was obtained for each curve, which indicates the copolymerization. The simple mixture of Polystyrene and HTT 1800 would result in a blend leading to two shifts in a DSC curve.

In Table 5.2 values of glass transition temperatures (Tg) for pure polystyrene and hybrid compounds are listed.

Table 5.2. Glass transition temperatures values for Styrene/ DCP 3 wt.%, Styrene 60 wt.%/HTT 1800 40 wt.%/DCP 3 wt.% bulk and Styrene 60 wt.%/HTT 1800 40 wt.%/DCP 3 wt.% solution polymerization

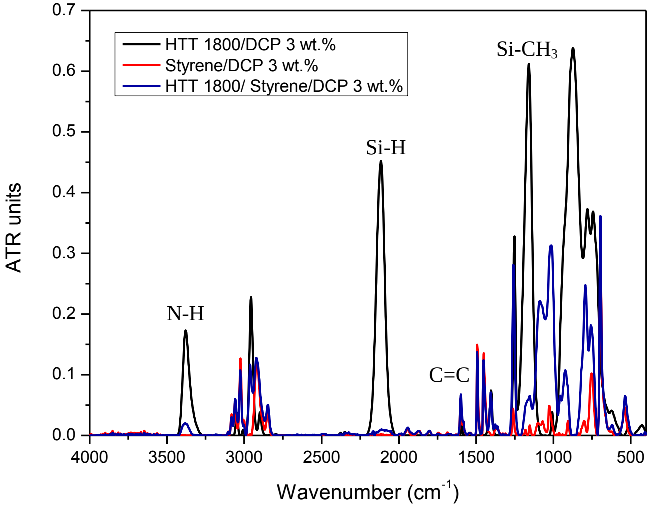
Sample	Tg (°C)
Styrene/DCP 3 wt.%	84
Styrene 60 wt.%/HTT 1800 40 wt.%/DCP 3 wt.% (solution polymerization)	91
Styrene 60 wt.%/HTT 1800 40 wt.%/DCP 3 wt.% (bulk polymerization)	102

A significant increase of glass transition was detected when pure polystyrene was compared to both styrene/HTT 1800 bulk and solution polymerization. The highest increase was observed for Styrene/HTT 1800 bulk polymerization. The lower Tg value for Styrene 60 wt.%/HTT 1800 40 wt.%/DCP 3 wt.% obtained by solution polymerization is due to the presence of solvent.

5.1.2 Fourier Transformed Infrared (FTIR)

To investigate the reaction between styrene and HTT 1800 FTIR was executed. The objective was to analyze reacting groups and remaining bonds. Results of the measurements are shown in Figure 5.6.

Figure 5.6 – FTIR measurements of styrene 60 wt.%/HTT1800 40 wt.%/DCP 3 wt.% obtained by bulk polymerization, pure crosslinked HTT 1800 and polystyrene.

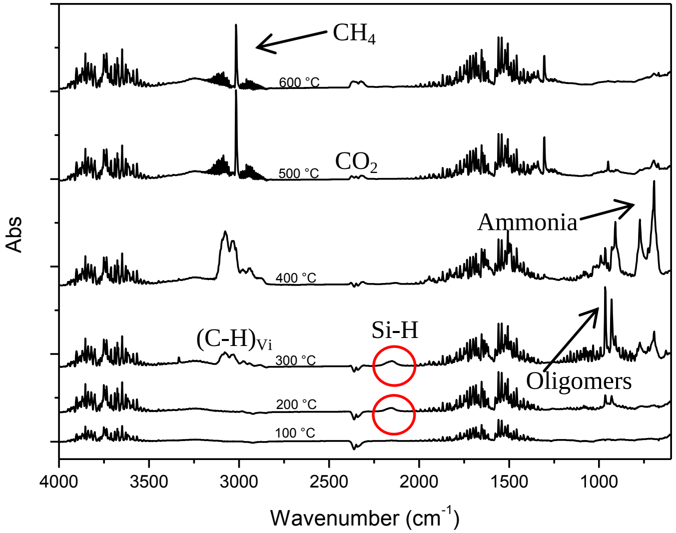


After reaction the consumption of vinyl group of styrene and HTT 1800 was expected. However no peak reduction of C=C from polystyrene was detected. This behavior leads to believe that C=C groups from HTT 1800 are, first of all, reacting with themselves and resulting in unreacted Si-H groups. These Si-H groups react preferentially with vinyl groups from styrene, although unreacted vinyl groups from C=C still remains. The last reaction occurs between C=C from styrene with themselves. Bearing in mind the difference of reactivity from both reactants, the methodology of reaction was planned to obtain the hybrid material with desired characteristics and based on previous reactivity test.

5.1.3 Thermogravimetric analysis monitored by Fourier Transformed Infrared (TGA-FTIR)

To investigate the gaseous products formed during pyrolysis of hybrid structures TGA-FTIR was executed. Respective FTIR spectra of the pyrolysis gases are shown in Figure 5.7. Due to the similarity of spectra from solution and bulk polymerization products only spectra of styrene 60 wt.%/HTT1800 40 wt.%/DCP 3 wt.% obtained by bulk polymerization are presented.

Figure 5.7 - TGA-FTIR of styrene 60 wt.%/HTT1800 40 wt.%/DCP 3 wt.% obtained by bulk polymerization.



Analyzing TGA-FTIR spectra at 200 °C a small peak occur around 2200 cm^{-1} related to liberation of Si-H. At 300 °C an absorbance peak related to $(C\text{-}H)_{vi}$ vinyl group liberation was detected at around 3000 cm^{-1}. In this region also oligomer release is detected at 1000 cm^{-1}. At 400°C were detected liberation of ammonia (N-H bonds), oligomers and vinyl group. The major weight loss occurs between 500 °C and 600 °C corresponding to the release of methane. The release of vinyl groups increase significantly from 300 °C to 400 °C. Usually this peak should appear at 300 °C and decrease due to crosslinking reactions (hydrosilylation or polymerization), although the increase of the signal for vinyl groups occurs due to the significant quantity of unreacted vinyl bonds. For a typical organic polymer TGA analysis the degradation starts at lower temperatures due to the weak thermal stability of organic materials. For the hybrid compounds an increased thermal stability due to the release of the vinyl groups at higher temperatures can be assumed. The liberation of unreacted vinyl groups containing compounds at high temperatures helps to understand the synthesis mechanism.

5.1.4 Preliminary conclusions

From free radical polymerization of styrene and HTT 1800 inorganic precursor it was expected to react vinyl groups from styrene and HTT 1800 to obtain strong covalent bonds between these two compounds. Due to the high reactivity of HTT 1800 with DCP and low reactivity of styrene with DCP at low temperatures, experimental procedure was modified to avoid premature reactions and total consumption of DCP radical by HTT 1800. From the performed analyses the following results can conclude:

- The obtained hybrid structure presents an improvement of thermal stability, leading to believe that covalent bonds were achieved;
- Glass transition temperatures increase, only one Tg for hybrid products was detected, indicating formation of an homogeneous structure;
- TGA-FTIR showed the increase of $(C\text{-}H)_{vi}$ release with the increment of temperature.

The results of the investigation leading to the questions, why this vinyl reaction did not occurred quantitatively between HTT 1800 and styrene? The answer for these questions is already discussed in literature.

Egorochkin et al. (1972) reported an effect called *dπ-pπ* interactions. Atoms like silicon, germanium and tin present a vacant *d* orbital in contrast to carbon, resulting in orbitals with energies close to those of the *s* and *p* orbitals in the outer electronic shell. Consequently organic compounds derived from this elements present chemical and physical properties untypical comparing to carbon analogues (same structure) due to the presence of the *d* orbital at the central atom (Pauling, 1947 in Egorochkin et al., 1972). This bond is formed when a substituent X in the M-X (M = Si, Ge, Sn or Pb) group is an atom with lone electron pairs (F, Cl, O, N, etc) or a groups with multiple bonds (CH_2=CH_2, HC=C-H, etc). The atom M will be an acceptor of the p electrons of atom X and the electron transfer will result in the formation of a dative *dπ-pπ* bond. Brockway and Wall, introduced the concept of partial double bonds involving *d* level of silicon but the first idea of *dπ-pπ* interactions was given by Pauling. According to Egorochkin et al., (1972) the degree of double bonding can then be considerable only in the presence of a partial positive charge at the silicon atom. Moreover, the degree of *dπ-pπ* interaction depends markedly on the steric disposition of the *d* orbitals relative to the σ bonds (Egorochkin et al., 1970).

The effect *dπ-pπ* on silicon atoms was also observed by quantum-chemical data indicating *dπ-pπ* interactions in Si-aryl and Si-vinyl bonds. Due to this effect, vinyl bonds from HTT 1800 present a different approach when compared to styrene vinyl bonds, turning difficult the occurrence of polymerization reaction.

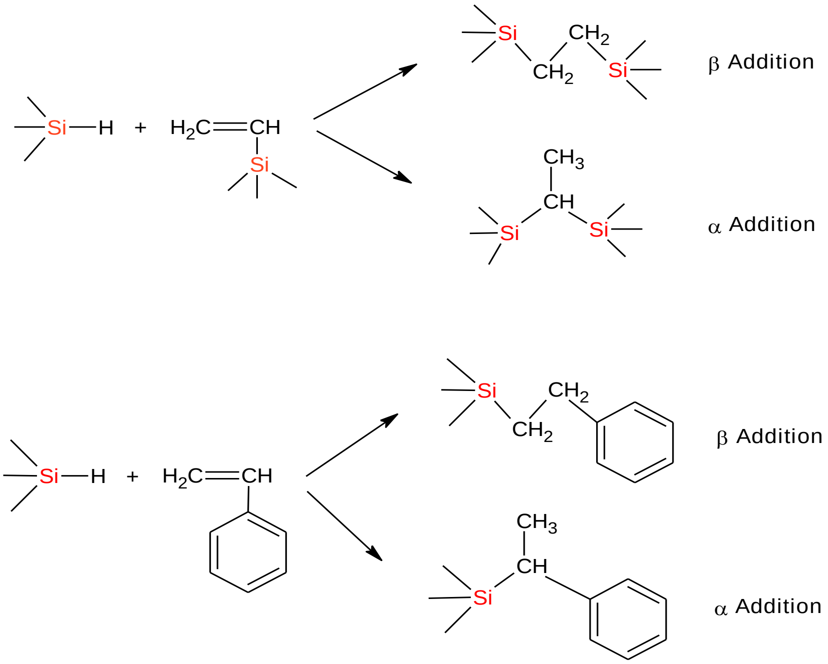
5.2 SYNTHESIS OF AN ORGANIC-INORGANIC HYBRID POLYMER USING PT CATALYST AND DICUMYL PEROXIDE BY SOLUTION POLYMERIZATION

Intending to improve the reactivity between the precursor and styrene leading to hybrid products with higher ceramic yield and modified properties another part of this work was the use of Pt catalyst. As previously discussed, hydrosilylation reactions have been extensively used to create new materials from Si-H and $H_2C=CH$ containing molecules. It is one of the most important laboratorial and industrial reactions for the preparation of silicon-based compounds. Besides radical initiator the reaction between vinyl bonds and Si-H bonds is generally promoted by a metal catalyst. The possibility to use both, vinyl and Si-H bonds increase the number of reacted groups increasing consequently the ceramic yield.

Follow this intention a hybrid polymer was synthesized by hydrosilylation reactions using styrene as organic monomer and two different precursors, HTT 1800 and ML 33. As a catalyst, Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane was applied. After hydrosilylation with the Pt catalyst, a radical initiator (dicumyl peroxide) was added also intending to react remaining vinyl groups from organic molecule and inorganic molecule to complete crosslinking reaction.

In Figure 5.8 displays the expected reaction mechanism.

Figure 5.8 – Expected hydrosilylation mechanism by using Pt catalyst.

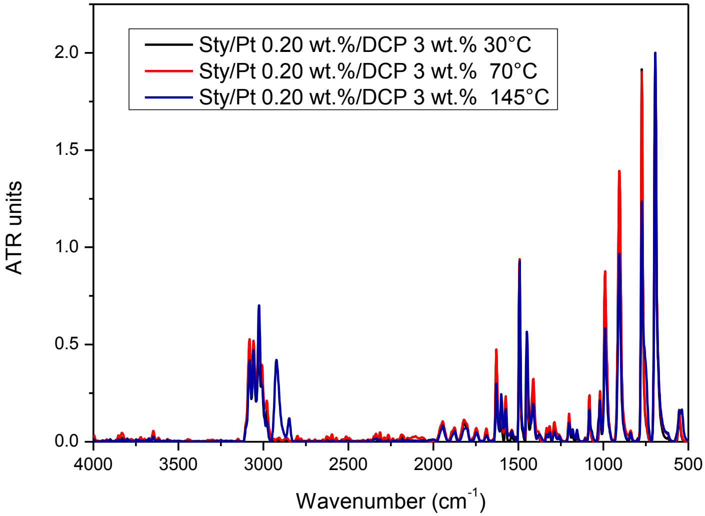


5.2.1 Fourier Transformed Infrared (FTIR)

FTIR analyses were executed to observe the influence of Pt catalyst on crosslinking reaction of organic monomer and inorganic precursor and to identify functional groups after reaction.

In Figures 5.9, 5.10 and 5.11 FTIR spectra are presented to investigate the reaction of styrene with HTT 1800 and ML33 in the presence of Pt catalyst depending on the temperature.

Figure 5.9 – Polymerization of styrene with Pt 0.20 wt.% catalyst and DCP 3 wt.% at different temperatures.



It was not observed any significant change in FTIR spectra, proving that styrene did not react with Pt catalyst. Although is it known that FTIR is a limited technique to observe yield information if reaction is not quantitatively.

Figure 5.10 – Polymerization of HTT 1800 with Pt 0.20 wt.% catalyst and DCP 3 wt.% at different temperatures.

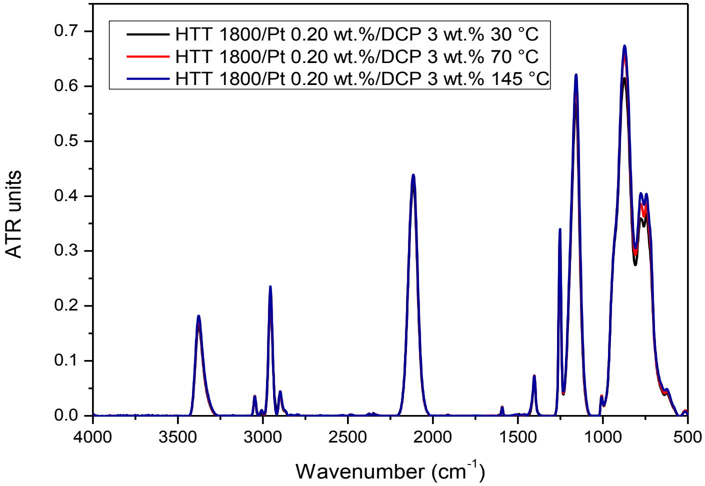
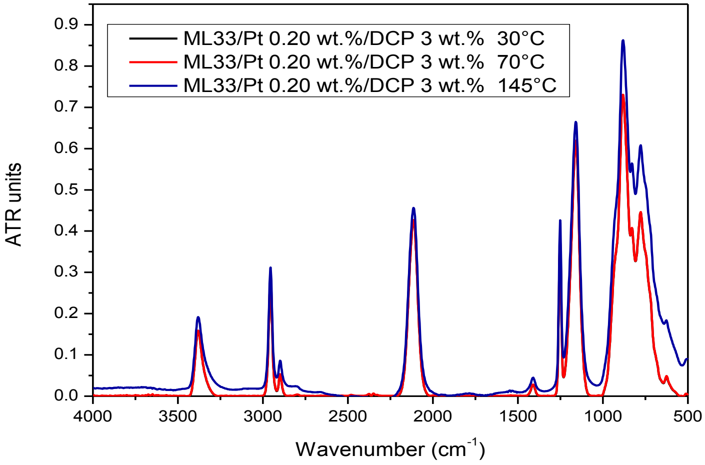


Figure 5.11 – Polymerization of ML33 with Pt 0.20 wt.% catalyst and DCP 3 wt.% at different temperatures.



For both inorganic precursors were not detected any significant changes in FTIR spectra. However observing HTT 1800 molecular structure is possible to see reactive Si-H and vinyl bonds. Some reaction between those groups in the presence of Pt catalyst could be expected although with FTIR technique presented no evidence. In Figure 5.12 and 5.13 are presented FTIR spectra from HTT 1800, Styrene, HTT 1800/Styrene and ML33, Styrene, ML33/Styrene, respectively

Figure 5.12 - FTIR spectra from HTT 1800/Pt 0.20 wt.% /DCP 3 wt.%, styrene/Pt 0.20 wt.% /DCP 3 wt.%, and styrene 60 wt.%/HTT 1800 40 wt.%/Pt 0.20 wt.% /DCP 3 wt.% performed at 135 °C.

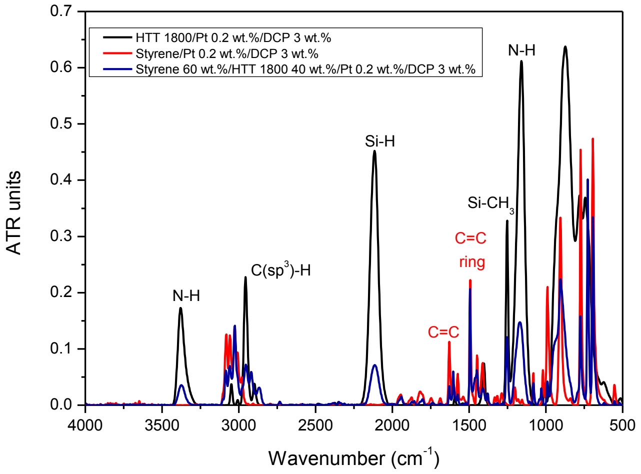
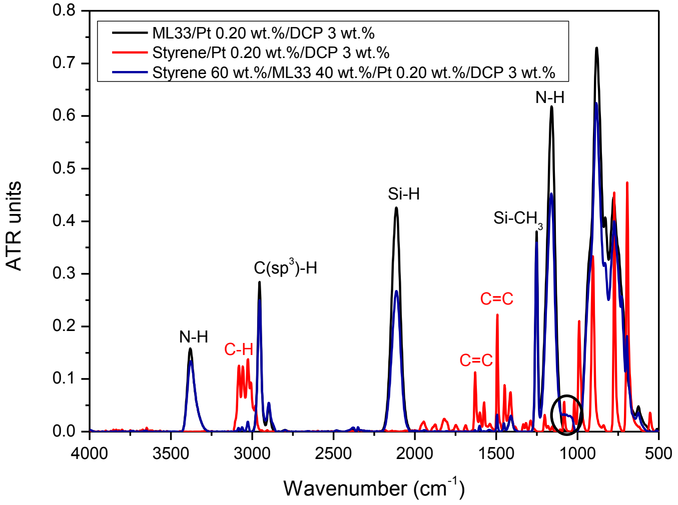


Figure 5.13 - FTIR spectra from ML33/Pt 0.20 wt.% /DCP 3 wt.%, styrene/ Pt 0.20 wt.% /DCP 3 wt.% and styrene 60 wt.%/ML33 40 wt.%/Pt 0.20 wt.% /DCP 3 wt.% performed at 135 °C.



In Table 5.3 functional groups and respective wavenumbers for Figure 5.12 and Figure 5.13 are listed.

Table 5.3 - Wavenumber and bonding type (Traßl, 2001; Yu et al., 1995; Bahloul et al., 1993; Gonsalves el at., 1992, Han et al., 1992; Burns and Chandra, 1989)

Wavenumber (cm^{-1})	Bonding type
3376	N-H, stretching
3081 - 3026	C-H, deformation
3025	C(sp^2)-H, deformation
2950	C(sp^3)-H, stretching
2112	Si-H, stretching
1629	C=C, stretching
1492	C=C, stretching
1252	Si-CH$_3$, deformation
1158	N-H, deformation

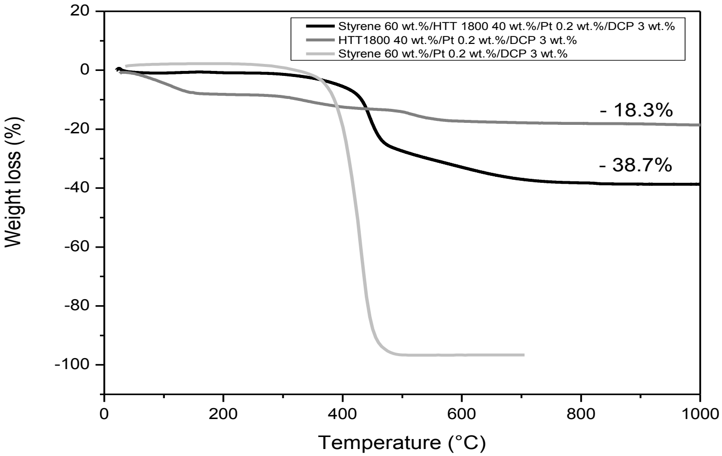
In Figure 5.12 and 5.13 the presence of groups from organic monomer and from precursors after reaction confirm that both reactants were into reaction. To characterize the reaction, some points are more important.

Observing spectra from products are noted a reduction in Si-H peak in 2212 cm^{-1}. This is an evidence that Si-H bonds were reacted with vinyl groups, also proved by the reduction of C=C bonds (1629 cm^{-1}). The reduction of N-H peak (3376 cm^{-1}) for HTT 1800/Styrene product is due to reactions between N-H and Si-H groups. However peaks related to Si-CH_2-CH_2- were expected to appear at 1100-989 cm^{-1}, the most complicated region to analyze. In Figure 5.12 and 5.13 are detected peaks from pure HTT 1800 and ML 33 in this region, not allowing identification of products.

5.2.2 Thermogravimetric Analyses (TGA) and oven pyrolysis

Termogravimetric analyses were executed to estimate the ceramic yield from products after the synthesis and compare with the ceramic yield obtained after heat treatment in an oven. Procedures concerning to TGA and oven analyses were described earlier. To perform those analyses protective atmosphere (Argon) was used. During TGA and oven analyses the synthesized polymers were pyrolysed and converted to ceramics. Results are presented in Figure 5.14 and 5.15.

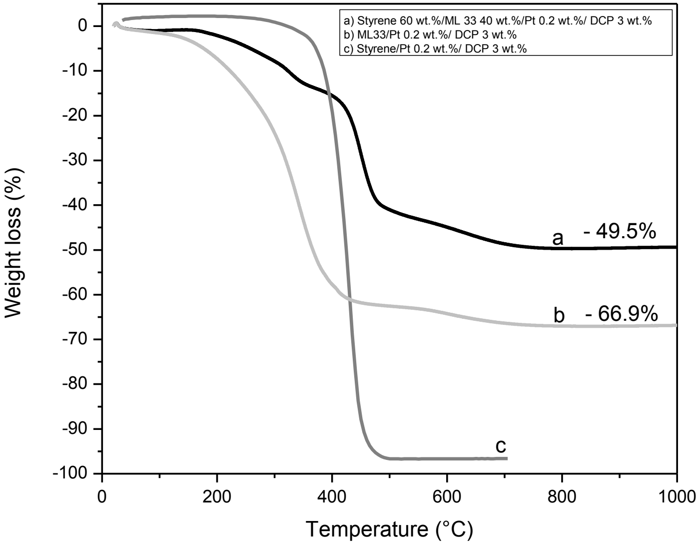
Figure 5.14 - TGA spectra from HTT 1800/Pt 0.20 wt.%/DCP 3 wt.%, styrene/Pt 0.20 wt.% /DCP 3 wt.% and HTT 1800 40 wt%/styrene 60 wt%/Pt 0.20 wt.% /DCP 3 wt.% performed at 135 °C.



Organic polymer polystyrene (styrene 60 wt.%/Pt 0.2 wt.%/DCP 3 wt.%) presented a weight loss of 100%, starting on approximately 263 °C and continuing until 484 °C due to the decomposition to gaseous and volatiles products. According Shapi (1990) the nature and amount of volatiles that can be observed depend strongly on the structure of polymer, the degradation conditions and methodology of analysis. Usually it is observed the liberation of styrene and its oligomers (dimers, trimers and tetramers).

HTT 1800 reacted with Pt and DCP yielding a high ceramic yield (around 82%). Although HTT 1800 weight loss starts extremely early (at around 76 °C) losing some oligomers and NH_3. From 250 °C to 500 °C the main gas release is ammonia as shown earlier by FTIR-TGA spectrum. At temperatures higher than 500 °C the release of methane was observed. During the pyrolysis and depending on the functional group of polysilazane chains, four different reactions can occur during the thermal treatment, leading to the crosslinked material: crosslinking via vinyl polymerization, hydrosilylation between Si-H and Si-vinyl groups, dehydrocoupling between Si-H and N-H groups and transamination (Flores et al., 2013). Observing the TGA from HTT 1800/Styrene product is possible to note a reduction on degradation steps, an increase of initial degradation temperature (starting around 320 °C) and a high ceramic yield, considering the ratio of HTT 1800 and styrene used. The major weight loss occurs between 400 and 700 °C. At this interval polymer changes to amorphous SiCN ceramic. It was expected at this point, the degradation of whole organic parts lead to the release of methane, H_2, small quantities of NH_3 and volatile compounds. Although due to increased formation of bonds between organic and inorganic part, was obtained a high ceramic yield. To prove this ceramic yield, an oven test was also performed to analyze the behavior of the material when submitted to a high temperature treatment. For HTT 1800 40 wt.%/styrene 60 wt.%/Pt 0.2 wt.%/DCP 3 wt.% sample the weight loss was 43.9%.

Figure 5.15 - TGA spectra from ML33/Pt 0.2 wt.% /DCP 3 wt.%, styrene /Pt 0.2 wt.% /DCP 3 wt.% and ML33 40 wt%/styrene 60 wt%/Pt 0.2 wt.%/DCP 3 wt.%.



The behavior of ML33/styrene product was unexpected. TGA spectrum for ML 33 reacted with Pt catalyst and DCP show a weight loss of 66.9% which is not a sufficient ceramic yield. Performing the synthesis between organic monomer and precursor ML 33 should be expected a weight loss between polystyrene and ML 33. However it was obtained a high ceramic yield and low weight loss. In oven test was obtained a weight loss of 48.6%.

Initially, hydrosilylation should be the reaction mechanism for styrene and ML 33, considering the following facts:

- The composition of ML 33 where 60% of bonds (Si-H) are totally available to react with vinyl groups from styrene;
- Initially, a low temperature reaction was used (30 °C) to avoid vinyl group thermal initiation maintaining the reaction viscosity lower and promoting high dispersion of solution;
- Lower reaction temperatures favoring hydrosilylation reaction and avoiding concurrent reactions.

Conclusions after hydrosilylation of HTT 1800 and styrene:

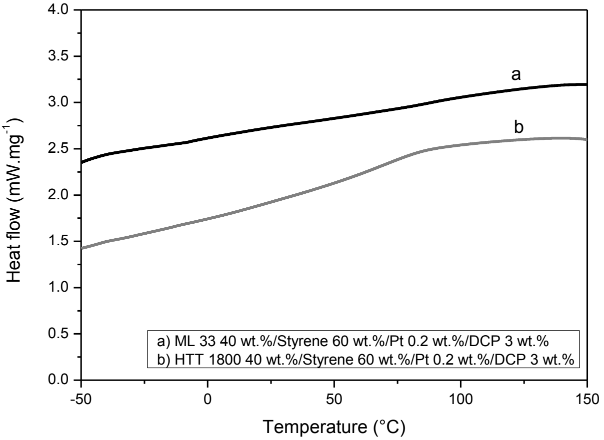
- HTT 1800 contains 20% of vinyl groups and 80% Si-H groups. Even performing synthesis at low temperatures to avoid thermal initiation of vinyl groups, those can react with vinyl bonds from styrene, resulting in steric hindrance from the beginning of reaction and increase in viscosity;
- Steric hindrance makes difficult to react all functional groups, forming networks not so strong with unreacted groups inside;

Considering cross linking reaction with dicumyl peroxide for both products, it should be a better reaction for HTT 1800/styrene once both reactants present vinyl groups. Although after hydrosilylation reaction a great number of vinyl groups were sterically hindered and the capacity of cross linking is reduced. Otherwise, the quantity of unreacted vinyl groups of ML 33/Styrene (and just from styrene) is sufficient to obtain a satisfactory cross linking and ceramic yield.

5.2.3 Differential Calorimetry Analyses (DSC)

Differential calorimetry analyses were performed to observe the behavior of glass temperature of hybrid structures. Figure 5.16 displays DSC spectra for HTT 1800/Styrene and ML 33/Styrene.

Figure 5.16 - DSC spectra for HTT 1800 40 wt.%/styrene 60 wt.%/Pt 0.2 wt.%/DCP 3 wt.% and ML 33 40 wt.%/styrene 60 wt.%/Pt 0.2 wt.%/DCP 3 wt.%.



DSC results from synthesized hybrid polymers present weak signals due to the high degree of crosslinking, resulting in a complex structure. For

ML 33/styrene it was impossible to observe the glass transition temperature, otherwise for HTT 1800/styrene the glass temperature was around 67 °C. As verified in TGA analyses the bonds formed between ML 33 and styrene appears to be stronger initially, probably resulting in less empty spaces inside structure, a better chain packing and higher Tg values. On the other hand, HTT 1800 and styrene present a higher ceramic yield probably due to the high capacity of crosslinking in the end of reaction by both reactants but in the beginning of synthesis these compounds are not capable of forming bonds to strong or a desirable structure packing. It is important to remember that the high viscosity presented earlier by HTT 1800 and styrene difficult the mobility of groups, avoids new interactions between active groups and reduces the conversion of products.

5.2.4 Determination of Gel Content

To analyze the crosslinking degree of hybrid polymer gel content was executed. For ML 33 40 wt.%/styrene 60 wt.%/Pt 0.2 wt.%/DCP 3 wt.% the gel content was around 50 % and for HTT 1800 40 wt.%/styrene 60 wt.%/Pt 0.2 wt.%/DCP 3 wt.% was about 80 %.

Table 5.4 – Gel content analysis.

Sample	**Precursor/Styrene wt. %**	**Gel content**
ML 33/Styrene	40/60	50 %
HTT 1800/Styrene	40/60	80 %

High gel content is obtained when the polymer formed present a high cross-linking degree and consequently insoluble products. The main reaction in styrene/ML 33 sample occurs between vinyl groups of organic monomer and Si-H groups of inorganic compound. The ML 33 capability of crosslinking it is not so pronounced as HTT 1800 precursor. Due to this, the hybrid product formed present a better solubility compared to styrene/HTT 1800 samples.

Styrene/HTT 1800 samples are capable to achieve a higher crosslinking degree due to the main formation of three dimensional networks instead low molecular weight compounds.

The formation of hybrid polymer is proven by the high gel content obtained when compared to the amount of styrene applied to both reactions, considering that, at the end of reaction the product weight obtained is almost the same weight of reagents. It is important to remember the total solubility of polystyrene in solvents.

5.2.5 Nuclear Magnetic Resonance Analyses (NMR)

To detect covalent bonds between organic monomer and inorganic precursor Nuclear Magnetic Resonance (NMR) was performed. Due to the low solubility of hybrid polymer solid state NMR was chosen instead liquid NMR.

5.2.5.1 ^{13}C solid state NMR

To analyze differences between pure precursor/catalyst/initiator and precursor/organic monomer/catalyst/ initiator solid state ^{13}C NMR was performed. In Figures 5.17 ^{13}C solid NMR spectra from pure HTT 1800 reacted with Pt catalyst and dicumyl peroxide is presented and in Table 5.5 are the most important chemical shifts from HTT 1800/Pt 0.2 wt.%/DCP 3 wt.%.

Figure 5.17 - ^{13}C solid NMR spectra from HTT 1800/Pt 0.2 wt.%/DCP 3 wt.%.

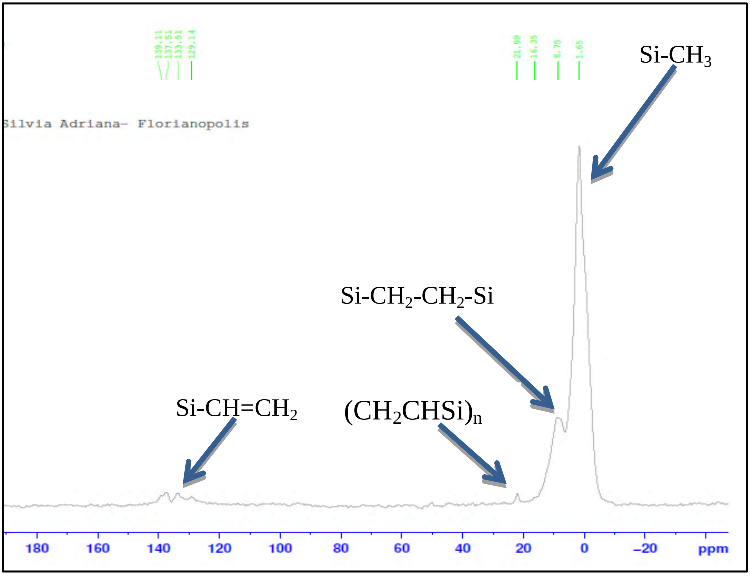


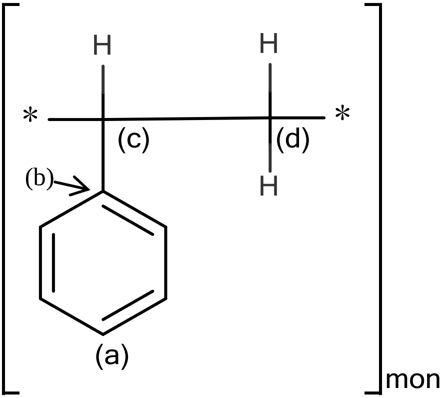
Table 5.5 - ^{13}C solid NMR chemical shift from HTT 1800/Pt 0.2 wt.%/DCP 3 wt.%.

Site	Chemical shift (ppm)
$Si\text{-}CH{=}\mathbf{C}H_2$	139.11
$Si\text{-}\mathbf{C}H{=}CH_2$	133.51
$(CH_2CHSi)_n$	21.99
$Si\text{-}\mathbf{C}H_2\text{-}\mathbf{C}H_2\text{-}Si$	9.75
$H_3\mathbf{C}\text{-}Si$	1.65

Comparing ^{13}C solid NMR spectra of pure HTT 1800 and HTT 1800 reacted with Pt catalyst and dicumyl peroxide with chemical shifts presented earlier to unreacted HTT 1800 reactions are detected between vinyl groups of HTT 1800. According the synthesis steps applied for pure HTT 1800 samples, firstly Pt catalyst (added at low temperatures) promotes hydrosilylation reactions between C=C and Si-H groups. Polymerization reactions involving HTT 1800 C=C bonds are also expected. With the increase of temperature and addition of DCP, the remaining unreacted vinyl bonds react with each other resulting in a complex and highly cross-linked three dimensional structure. Although, as already observed, molecular structure configuration of HTT 1800 can make difficult some types of reaction due to steric hindrance. Analyzing Figure 5.17 and Table 5.5 was detected signals at 1.65 ppm indicating the presence of $H_3C\text{-}Si$ bonds, 139.11 ppm and 133.51 ppm related to remaining $Si\text{-}CH{=}CH_2$ groups. The most interesting chemical shifts were at 21.99 ppm related to the polymerization of C=C bonds $(CH_2CHSi)_n$ and 9.75 ppm associated to the hydrosilylation between C=C and Si-H groups ($Si\text{-}CH_2\text{-}CH_2\text{-}Si$).

The characterization of HTT 1800 and styrene homopolymers was important to understand which chemical shifts should continue appearing in hybrid structure and where should be located new chemical shifts responsible to prove covalent bonds of organic-inorganic compound. In Figure 5.18 visualize carbon atoms identified in ^{13}C NMR. Carbons from ring were represented by (a) and showed a chemical shift at around 128 ppm, carbon (b) at 145 ppm, carbon (c) at 40 ppm and carbon (d) at 35 ppm. A prediction of results was also performed using the prediction software, Mnova Suite from Mestrelab Research. The chemical shifts obtained with prediction software were: carbon (a) at around 128 ppm, carbon (b) at 143 ppm, carbon (c) at 40 ppm and carbon (d) at 35 ppm.

Figure 5.18 – Styrene monomer structure



For the two steps reaction involving organic monomer and precursors using Pt catalyst and dicumyl peroxide, hydrosilylation (at low temperatures) was expected as the first reaction between Si-H and vinyl groups. At the end a crosslinking reaction of unreacted vinyl bonds from organic monomer and precursors promoted by dicumyl peroxide is probable. In solid state ^{13}C NMR was expected to visualize a displacement of chemical shifts from carbons (c) and (d) to the right due to the reaction between Si-H and C=C. Bearing in mind that Si atoms present a lower electronegativity when compared to C atoms, consequently electrons in the C-Si bonds are very close to the carbons in this compound. The result is a carbon nuclei shielded from the external magnetic field and reduced chemical shifts values of carbons (c) and (d).

In Figures 5.19 and 5.20 and Tables 5.6 and 5.7 are presented ^{13}C solid state NMR spectra of HTT 1800/styrene and ML 33/styrene and chemical shifts, respectively.

Figure 5.19 – ^{13}C solid state solid NMR spectra from HTT 1800 40 wt.%/styrene 60 wt.%/Pt 0.2 wt.%/DCP 3 wt.%.

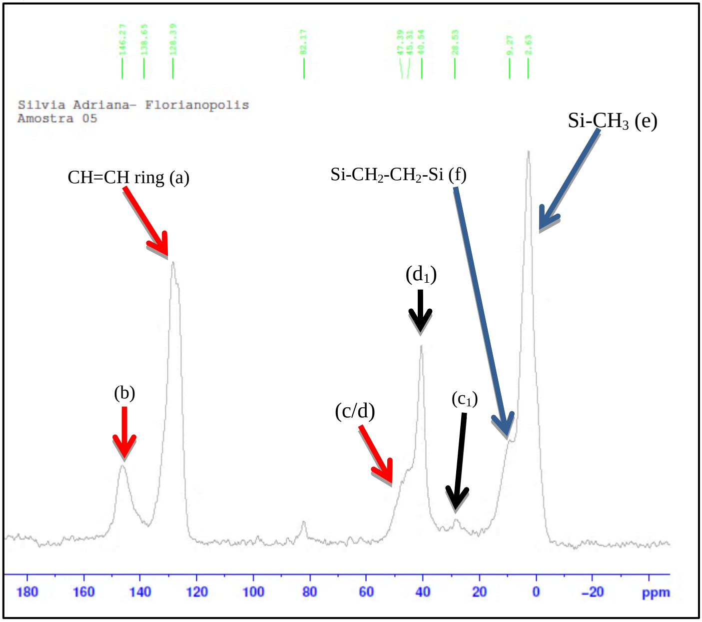
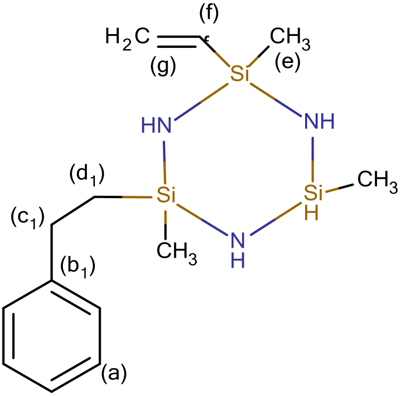


Table 5.6 - ^{13}C solid state NMR chemical shift from HTT 1800 40 wt.%/styrene 60 wt.%/Pt 0.2 wt.%/DCP 3 wt.%.

Site	**Chemical shift (ppm)**
CH$_{(b)}$ Styrene (Styrene)	146.27
Si-CH=**CH**$_2$ (HTT 1800)	138.65
CH=CH/Ring (Styrene)	128.39
d (polystyrene)	47.39
c (polystyrene)	45.31
d$_1$ (Hybrid)	40.54
c$_1$ (Hybrid)	28.53
Si-CH$_2$-CH$_2$-Si (HTT 1800)	9.27
H$_3$C-Si (HTT 1800)	2.63

It is evident from Figure 5.19 and Table 5.6 that was not obtained a pure hybrid structure. Chemical shifts of polystyrene homopolymer (47.39 ppm, 45.31 ppm) and remaining unreacted C=C bonds (138.65 ppm) from HTT 1800 were detected. Although was noted a reduction in the intensity of the Si-CH$_2$-CH$_2$-Si peak (9.27 ppm) related to the hydrosilylation between HTT 1800 groups (C=C and Si-H) indicating that the hydrosilylation probably occurred also with styrene C=C bond. The most interesting result was two new chemical shifts at 40.54 ppm attributed to the shielding of carbon (d) (and now represented by d_1) and at 28.53 ppm attributed to the shielding of carbon (c) (now represented by c_1). Figure 5.20 represents the proposed hybrid structure for HTT 1800/styrene product.

Figure 5.20 – Hybrid HTT 1800/styrene proposed structure.



A ^{13}C NMR prediction was also performed with the proposed structure. The chemical shifts observed were at 143 ppm related to carbon (b), 37 ppm related to carbon (d) and 29 ppm related to carbon (c), confirming ^{13}C NMR measured and proposed structure.

The same analysis was performed to ML 33 and styrene products. The only difference is the absence of C=C bonds in ML 33 structure. In this case were not observed chemical shifts from $Si-CH=CH_2$ (at around 138 ppm) and from $Si-CH_2-CH_2-Si$ (at around 9 ppm). In Figure 5.21 and Table 5.7 results are exhibited.

Figure 5.21 - ^{13}C solid state NMR spectra from ML 33 40 wt.%/styrene 60 wt.%/Pt 0.2 wt.%/DCP 3 wt.%.

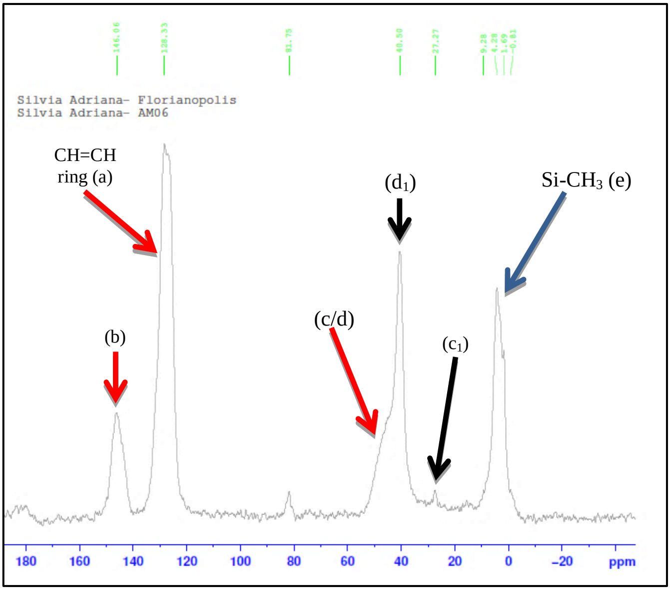
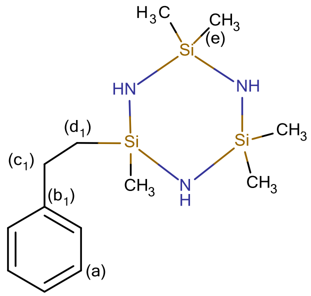


Table 5.7 - ^{13}C solid state NMR chemical shift from ML 33 40 wt.%/styrene 60 wt.%/Pt 0.2 wt.%/DCP 3 wt.%.

Site	Chemical shift (ppm)
$CH_{(b)}$ Styrene (Styrene)	146.06
CH=CH/Ring Styrene	128.33
c/d (polystyrene)	Around 50.00
d_1(Hybrid)	40.50
c_1 (Hybrid)	27.27
H_3C-Si	4.28

Chemical shifts from polystyrene homopolymer and precursors were detected. However the chemical shifts attributed to the hydrosilylation reactions between inorganic precursor and styrene were detected. The two chemical shifts are: at 40.50 ppm attributed to the shielding of carbon (d) (and now represented by d_1) and at 27.27 ppm attributed to the shielding of carbon (c) (now represented by c_1). In Figure 5.21 is represented a proposed hybrid structure for HTT 1800/styrene product.

Figure 5.22 – Hybrid ML 33/Styrene proposed structure.

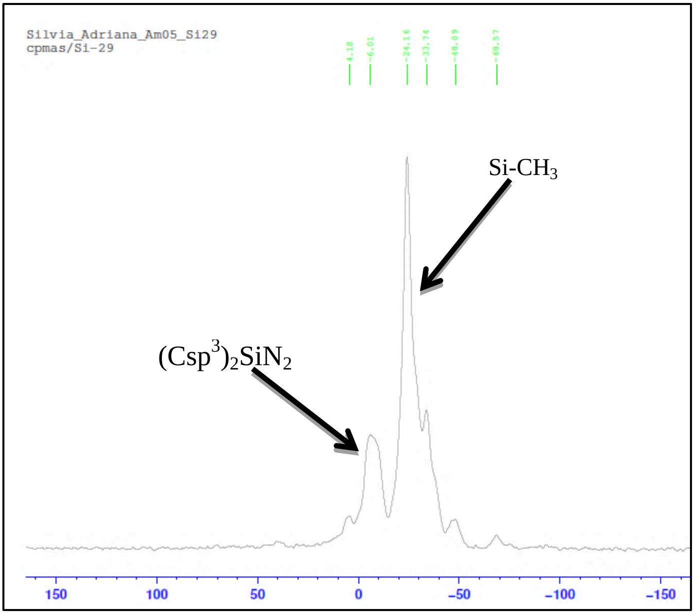


For ML 33/styrene a ^{13}C NMR prediction was also performed with the proposed structure. The chemical shifts observed were at 143 ppm related to carbon (b), 38 ppm related to carbon (d) and 29 ppm related to carbon (c), confirming ^{13}C NMR measured and proposed structure.

5.2.5.2 ^{29}Si solid state NMR

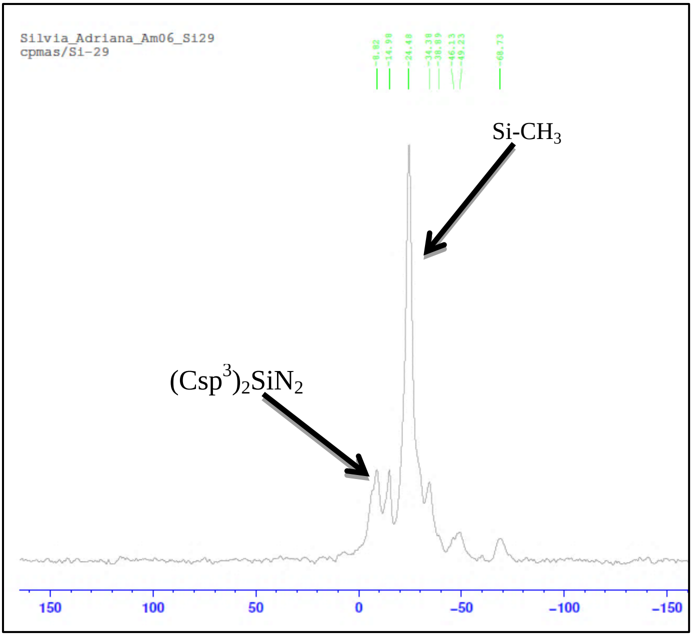
Intending to investigate more about possible bonds formed in hybrid structures ^{29}Si solid state NMR was performed. In Figures 5.23 and 5.24 are presented spectra from HTT 1800/styrene and ML33/styrene, respectively.

Figure 5.23 - ^{29}Si solid state NMR spectra from HTT 1800 40 wt.%/styrene 60 wt.%/Pt 0.2 wt.%/DCP 3 wt.%.



The ^{29}Si solid state NMR is helpful to detect reactions between Si-H and N-H bonds and possible unreacted remaining groups. As already expected the Si-CH_3 bond was detected at -24.14 ppm. The chemical shift related to Si(CH_3)(CH=CH_2) at -14.8 ppm disappear indicating complete reaction of these sites. Chemical shift from $(Csp^3)_2SiN_2$ was detected at -6.01 ppm.

Figure 5.24 - ^{29}Si solid state NMR spectra from ML 33 40 wt.%/styrene 60 wt.%/Pt 0.2 wt%/DCP 3 wt.%.



ML 33/styrene ^{29}Si NMR shows the Si-CH_3 bond at -24.48 ppm and $(Csp^3)_2SiN_2$ detected at -8.82 ppm. Although it is complicated to confirm hybrid reaction through ^{29}Si NMR in both products due to the difficulty to differentiate and identify Si atoms connected to CH_2CH_2Ph from styrene.

To both products was executed the ^{29}Si NMR prediction using Mnova software. For HTT 1800/Styrene sample results only indicated two peaks at around -8 ppm related to CH_2SiN_2 and at around -15 ppm related to N_2SiCH_3. For ML 33/Styrene sample results showed two peaks between 0 and -10 ppm related to CH_2SiN_2 and N_2SiCH_3. Unfortunately NMR prediction was not useful to estimate and confirm the hybrid structure.

5.2.6 Preliminary Conclusions

The synthesis using Pt catalyst and dicumyl peroxide as a radical initiator was successful to obtain hybrid polymers with significant ceramic yield. The main difference between synthesis A and B to synthesis C and D was the use of Pt catalyst in the beginning of the reaction. The objective was to promote, first of all, the hydrosilylation reaction between vinyl groups from styrene and Si-H groups from HTT 1800. Subsequently dicumyl peroxide was added to consume the unreacted vinyl groups from styrene and HTT 1800 and result in a higher crosslinking degree.

^{13}C NMR analysis was effective to show the formation of hybrid structure, proved also with a NMR software predictor. More conclusive results about thermal improvement were displayed by TGA measurements confirming the capability of hybrid polymer to attain higher ceramic yields. FTIR, gel content and DSC analysis were a support to understand mechanism behavior. ^{29}Si NMR analysis was not so conclusive due to the difficulty to perform this type of measurements and the complexity of hybrid structure obtained.

6. CONCLUSIONS

Free radical bulk and solution polymerization was expected to be a good synthesis route to develop hybrid organic-inorganic compounds from styrene and HTT 1800 due to the presence of vinyl groups in both reactants. Results obtained were considered satisfactory, thermal efficiency was sufficient to classify this structure as a preceramic material. Nevertheless results allowed understanding why higher ceramic yield, previously expected, was not obtained. In literature explanation about the low reactivity of HTT 1800 vinyl groups with vinyl groups from styrene was available. Results from synthesis A and B proved in a satisfactory way the *dπ-pπ* interactions theory.

The second part of this work related to hydrosilylation reactions using platinum catalyst and a free radical initiator to consume unreacted remaining groups presented interesting results. The synthesis route used proves to be efficient to obtain a hybrid product with improved thermal stability and sufficient ceramic yield. Covalent bonds were achieved between organic and inorganic molecules using platinum catalyst, consequently promoting bonds not obtained by the first methodology applied.

However further confirmation about the nature of chemical bonds of hybrid structure are necessary to define better the synthesis mechanism and to improve the reaction. The products obtained contain organic-inorganic hybrid polymers and an undesired mixture of organic and inorganic homopolymers. The quantification of mixture degree and phases separation may help to achieve different characteristics of final products.

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