FUNCTIONALIZED SILICON POLYMERS: NOVEL MATERIALS FOR CATALYSIS

Thesis submitted to

Cochin University of Science and Technology

in partial fulfillment of the requirements

for the Degree of

Doctor of Philosophy

in

Chemistry

Under the faculty of Science

By

MANGALA K

DEPARTMENT OF APPLIED CHEMISTRY

COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY

KOCHI-22, INDIA

September 2011

DEPARTMENT OF APPLIED CHEMISTRY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI - 682 022, INDIA
Phone : 0484-2575804, Telex : 885-5019 CU IN, Grams : CUSAT
Fax : 91-484-2575804, E-mail : chem@cusat.ac.in Web: www.cusat.ac.in/dac

Certificate

This is to certify that the thesis entitled "**Functionalized Silicon Polymers: Novel Materials for Catalysis"** submitted for the award of the Degree of Doctor of Philosophy of Cochin University of Science and Technology, is a record of original research work carried out by Mrs. Mangala K. under my supervision and guidance in the Department of Applied Chemistry, and further that it has not formed the part of any other thesis previously.

Kochi-22
16/09/2011

Dr. K. Sreekumar
(Supervising Guide)

DECLARATION

I hereby declare that the thesis entitled “**Functionalized Silicon Polymers: Novel Materials for Catalysis”** submitted to Cochin University of Science and Technology for Ph. D. Degree, is based on the original work done by me under the guidance of Dr. K. Sreekumar, Professor, Department of Applied Chemistry, Cochin University of Science and Technology and further that it has not previously formed the basis for the award of any other degree.

Kochi-22 **Mangala K**

16/09/2011

"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"

Marie Curie

Dedicated to

Aravind

Acknowledgement

This thesis would not have been possible without the sincere co-operation of others. I express my sincere gratitude to them at this juncture.

Dr. K. Sreekumar, my supervising guide and Head of the Department for his valuable advice, persistent encouragement and guidance.

Dr. K. Girish Kumar, former Head and my doctoral committee member for his suggestions and support.

Dr. M. R. Prathapachandra Kurup, former Head of the Department for providing the necessary facilities in the Department.

All other faculty members, administrative staff and librarian for their pertinent support.

All my teachers, those who helped to expand my perception

Rajesh, Suresh, Kannan, Mahesh,Elizabeth, Anoop, Jiby, Smitha, Sinija,Sherly Mole, Jabia, Jithin, Sumesh, Anjali, Smruthi, Saritha- My dear labmates and friends for their co-operation and encouragement.

Friends of Department of Applied Chemistry

My friends Jaseer, Leena, Rekhasree for their help and support.

Friends of Department of Physics, Polymer Science and Rubber Technology

NMR Research Centre, IISc, Bangalore for NMR spectral analysis

SAIF, STIC-CUSAT for various spectral analysis

Süd-chemie-Cochin for Surface area analysis

Dr. R Ramesh, Bharathidasan University, Trichy for EPR analysis

CUSAT, CSIR-Delhi for financial support.

My dear friends Sheeba Rajesh and Sini Binoj for their love and support.

Aravind, my dear husband who was always with me.

Vaishnav my dear son

My family for their love and support

Finally I thank ***God*** *for his blessings*

Mangala

PREFACE

The development of polymer supported catalysts can be considered as an advancement for attaining one of the major goals of 'green chemistry', ie, to facilitate efficient recovery of the catalyst from the reaction products, there by reducing inorganic waste.

Polycarbosilanes (PCS) a rather neglected class of polymers has attained considerable interest recently. This class of polymers can be compared to the existing classes of inorganic and organic polymers, they possess a combination of low t_g's and high synthetic versatility similar to polyphosphazenes and polysiloxanes and with good chemical backbone stability similar to that of polyolefins. Polycarbosilanes can represent structural hybrid between polysilanes and polyolefines, which have found applications as liquid crystals, SiC-precursor and catalyst support.

By introducing transition metal ions to polycarbosilanes, we can create functional polymer with properties such as catalytic activity. The immobilization of transition metal ions on polymer supports offers a number of advantages over solution phase chemistry. In an ideal case, the supported complexes can be recovered from reaction mixtures by simple filtration, they also do not contaminate the product solution, they can be recycled, and they can help in increasing the selectivity

Relatively few examples of metal- functionalized polycarbosilanes have been reported. In a reaction, the functionalized macromolecules with bound catalytic centers surrounded by solvents fulfil the function of isolated micro reactors. The high surface area of the polycarbosilane increases the rate of the reaction.

Dendrimers are monodispersed nanosized polymeric molecules composed of two or more tree like dendrons. Dendritic molecules are repeatedly branched species that are characterized by their structure perfection. Dendrimers are mainly used in the area of catalysis and in biotechnology and medicine. Dendrimers are considered to fill the gap between homogeneous and heterogeneous catalysts. The dendrimer functionalized polymers can be used as heterogeneous catalyst.

Objectives of the present study

1 Synthesis and characterization of polycarbosilanes.
2 Incorporation of metal ions on polycarbosilanes and their characterization.
3 Study of the catalytic activity of metal ion incorporated polycarbosilanes.
4 Synthesis and characterization of polysilane functionalized with PPI dendrimer.
5 Study of the catalytic activity of PPI dendrimer immobilized polysilane.

Thesis comprises of six chapters

In the first chapter, literature review about polymer supported metal catalysts is presented. This chapter also includes a thorough review of silicon polymers, particularly polycarbosilanes.

The second chapter mainly discusses about polycarbosilanes and their synthesis. Polycarbosilanes are organic-inorganic hybrid polymers which have both Si and C in their back bone structure; they have been of exacting significance as potential precursor to SiC. Polycarbosilanes have variety of possible applications that are opening up for these hybrid polymers in the areas such as nanotechnology, surface science, bio-medicine, catalysis, electrochemistry, liquid crystals, new ceramic materials, organic hybrid materials and nanocomposites. Many of these play dominant roles in the development of science in the twenty first century, and we have no doubt that silicon will occupy a prominent position in all of them as well. Five polycarbosilanes were synthesized from corresponding monomers, trichloromethylsilane, chlorodimethylvinylsilane, diethoxymethylvinylsilane and trimethoxyvinylsilane. Homopolymers with trichloromethylsilane, diethoxymethylvinylsilane and copolymers with trichloromethylsilane in combination with chlorodimethylvinylsilane, diethoxymethylvinylsilane, trimethoxyvinylsilane were prepared. The preparation involved the Wurtz-type coupling reaction of monomer molecules in the presence of metallic sodium. Characterization of the prepared polycarbosilanes by various spectroscopic techniques such as UV-Vis DRS, FT- IR, ^{29}Si-CP-MAS NMR, solid state- ^{13}C NMR spectroscopy, TG-DTA, BET surface area analysis and X- ray diffraction analysis is also presented. Halogen estimation was done by Volhard method. From the results of analytical data the structure of polycarbosilanes were established. All the prepared polycarbosilanes are of highly cross-linked structure and amorphous in nature. All of them possess high temperature stability and high surface area. The polycarbosilanes, except PCS 5, are capable of further functionalization since they have at least one chlorine substituent.

The third chapter deals with the synthesis and characterization of metal ion immobilized polycarbosilanes. The nucleophilic substitution reaction has been used to add side chains or to modify the structure of initially obtained polycarbosilane through reaction with Si-Cl or Si-OR groups on the polymer back bone. Polycarbosilanes formed by the polymerization of monomers such as trichloromethylsilane, chlorodimethylvinylsilane, diethoxymethylvinylsilane and trimethoxyvinylsilane were used for the incorporation of metal ions. The metal ions selected were Ti(IV), Mn(II), Co(II), Ni(II), Cu(II) and Pd(II). Metal ion incorporated polycarbosilanes were characterized using various analytical methods. The spectroscopic techniques used are FT-IR, UV-Vis DRS, ^{29}Si-CP-MAS NMR, ^{13}C CP-MAS NMR and EPR spectroscopy. Thermal behaviour was analysed by TG/DTA. Magnetic susceptibility measurements, BET surface area analysis were used to analyse the properties of metal ion incorporated polycarbosilanes. Metal ions were estimated with AAS/ICP-AES. Factors influencing metal incorporation were studied in detail.

Chapter four deals with the detailed study of the catalytic activity of polycarbosilane supported transition metal ions. Transition metals have important role as catalysts in organic synthesis. Metal ion incorporated polycarbosilanes were used as catalysts for different organic reactions. Four different types of reactions were taken into consideration viz, Mannich reaction, Knoevenagel Condensation Reaction, Biginelli reaction and Heck reaction. Reaction conditions were optimized. The purity of the reaction products was checked by means of HPLC and characterized with ^{1}H NMR, LC-MS and FT IR spectroscopic techniques and melting point.

Fifth chapter includes the discussion about dendrimers and polymer supported dendrimers and their preparation. This chapter discusses about the preparation of dendrimer functionalized polysilane. Polysilane was synthesized from the monomer, trichloromethylsilane. The polysilane was characterized by GPC, FT- IR, ^{29}Si-CP-MAS NMR and ^{13}C CP-MAS NMR spectroscopy. The polysilane supported PPI dendrimer was prepared by divergent method and dendrimer upto the third generation was prepared.

Michael addition and reduction were used to synthesize PPI dendrimer. The polysilane functionalized with dendrimer was characterized by FT-IR, ^{29}Si-CP-MAS NMR, ^{13}C NMR spectroscopy and amino group estimations were carried out in each generation. The catalytic activity of PPI dendrimer immobilized polysilane was studied. Knoevenagel Condensation Reaction was selected to study the catalytic activity. Reaction conditions were optimized.

The final chapter presents the summary and important conclusions of the thesis.

Contents

Chapter 1

INTRODUCTION: POLYMER SUPPORTED CATALYSTS

Contents

1.1. Polymers as heterogeneous supports for catalysts

The revolutionary approach behind solid phase synthesis as considered by Merrifield in 1963 is that, if the peptide is attached to an insoluble support, then any unreacted reagents left at the end of the reaction can be removed by a simple wash procedure, greatly decreasing the time required for synthesis.[1]

In modern synthetic organic chemistry, the development of efficient reagent or catalyst recycling systems is regarded as one of the most important topics.[2-4] The use of polymer supports is one of the potential approaches for this purpose, and the immobilization of reagents or catalysts on polymer supports offers a number of important advantages over their traditional homogeneous counterparts.[5-16] For example, their separation from reaction products is easy and their potentiality for the consecutive recycling steps is accessible for a green chemical process. In addition, the immobilization on polymeric supports often causes the stabilization of sensitive catalyst and provides the potential applicability to smart materials. Interest in the development of environmentally benign synthesis has evoked a renewed interest in developing polymer-supported metal catalysts and reagents for organic synthesis that maintain high activity and selectivity.[17] The immobilization of transition metals on polymer supports offers a number of advantages over traditional solution-phase chemistry. In an ideal case, the supported complexes can be recovered from reaction mixtures by simple filtration, they do not contaminate the product solution, they can be recycled, and they can help increase selectivity. As transition-metal salts are often expensive to purchase, the immobilization on a support, thereby enabling simple extraction and recyclability, makes for commercial advantage as well as ease of manipulation. Supported catalysts have also been used for rapid production of compound libraries.[18]

Regardless of these advantages, solid-phase catalyst is commonly difficult to retain or raise the activities relative to their homogeneous counterparts. Because of this significant disadvantage, solid-phase reaction system does not maintain its synthetic utility in many cases. On the other hand, the use of functionalized polymers to provide an effective reagent or catalyst recycling system has gained attention as an efficient alternative that avoids the use of expensive ionic liquids or fluorous solvents.[10,19-21] There are however a number of disadvantages including the fact that often there is metal leaching during the course of a reaction and they are often not recyclable. In addition, when considering asymmetric synthesis, the enantioselectivity of polymer-supported complexes can be less than that of the homogeneous analogue.

Usually amorphous and ordered silicas, clays, and highly crosslinked polymers are used as the supports to create a heterogenous catalyst from a homogeneous catalyst. The principal immobilization mechanisms consist of ligand grafting, metal coordination, microencapsulation, electrostatic interactions, and ion exchange.

As a result, much of the recent work has been focused on developing and screening new polymer supports for attachment of metals and on developing methods for increasing activity and selectivity. Also, there has been an increase in reports presenting the use of combinatorial methods to discover new catalysts. Over the past few years there have been a large number of reviews on solid-supported catalyst and reagent chemistry including the recent major review of Ley and co-workers[22,23].

Nearly half a century ago, Merrifield reported the concept of solid-phase synthesis using heterogeneous chloromethylated polystyrene that was lightly cross-linked by divinylbenzene, known as Merrifield resin (Figure 1),[1] and since then the use of polymers in various ways to facilitate synthesis and product purification has become widespread.

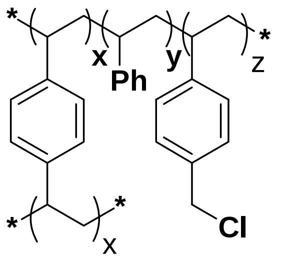


Figure 1: Merrifield Resin

While heterogeneous polystyrene such as Merrifield resin remains a workhorse in the field of polymer assisted synthesis as a support for not only solid-phase synthesis but also reagent and catalyst immobilization as well, many other macromolecular materials have also been used. Therefore, it is reasonable to expect that since the structure of a polymer and its properties can impact different chemical reactions in various ways,[7] no single polymer structure would be optimal for every imaginable synthetic application. In fact, this idea was recognized early on in the field of solid-phase peptide synthesis because Merrifield resin is only poorly compatible with highly polar solvents commonly used in traditional peptide synthesis, such as DMF.[24-26] The poor solvent absorbing and swelling properties of Merrifield resin and its derivatives in polar solvents led Bayer to use soluble poly(ethylene glycol) (PEG, Figure 2) as the support in what he referred to as liquid-phase synthesis[27] and to add PEG grafts to the cross-linked polystyrene core of Merrifield resin.[28]

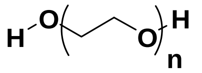


Figure 2: Poly (ethylene glycol)

While the use of PEG as a support for peptide synthesis is no longer common, the polystyrene-PEG composite material Bayer introduced is widely used today and is known as Tentagel (Figure 3).

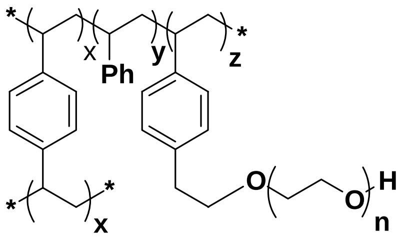


Figure 3: Tentagel

This material has an advantage over Merrifield resin in that the point of synthesis is moved away from the nonpolar polystyrene backbone of the resin bead to the ends of the polyether grafts, and because of this, the need for the resin swelling is reduced. Many other groups also made significant early contributions to this field and studied a large number of other polymers in various formats for use, not only as platforms for peptide synthesis but also both for organic molecule synthesis, in general and as carriers of reagents and catalysts for reacting with unanchored synthetic substrates.[29] Contributors to this field include Merrifield, Sheppard, Sparrow, Arshady, Meldal, Sherrington, Letsinger, Gletting, Barany, Rapp, the team of Gooding, Labadie, and Porco, Andrus, Buettner, Adams, Hoeprich, Rodda, Zhao, Lebl, and Daniels, who discussed their own research regarding the use various macromolecular materials, such as polyalkenes, polyethers, cotton, glass, etc., in numerous formats, including beads, surfaces, membranes, etc, for facilitating synthesis.[30] Additionally, the range of soluble polymers used in this context has been reviewed by both Bergbreiter[31,32] and Janda.[33,34] The discussion about the recent work in the field of developing versatile polymer supports for organic synthesis, mainly based on the structure of the polymer backbones and the type of monomer used to prepare them, rather than on the physical or chemical properties of the materials or the types of compounds attached to them. Hybrid materials such as Tentagel that are combinations of two different polymers grafted together are discussed along with the unanchored polymer that corresponds to the graft where the synthetic substrate, reagent, or catalyst is attached, rather than the polymer used to anchor the graft, since it is the polymer closer to the action and presumably exerts greater influence on the chemistry being performed.[30]

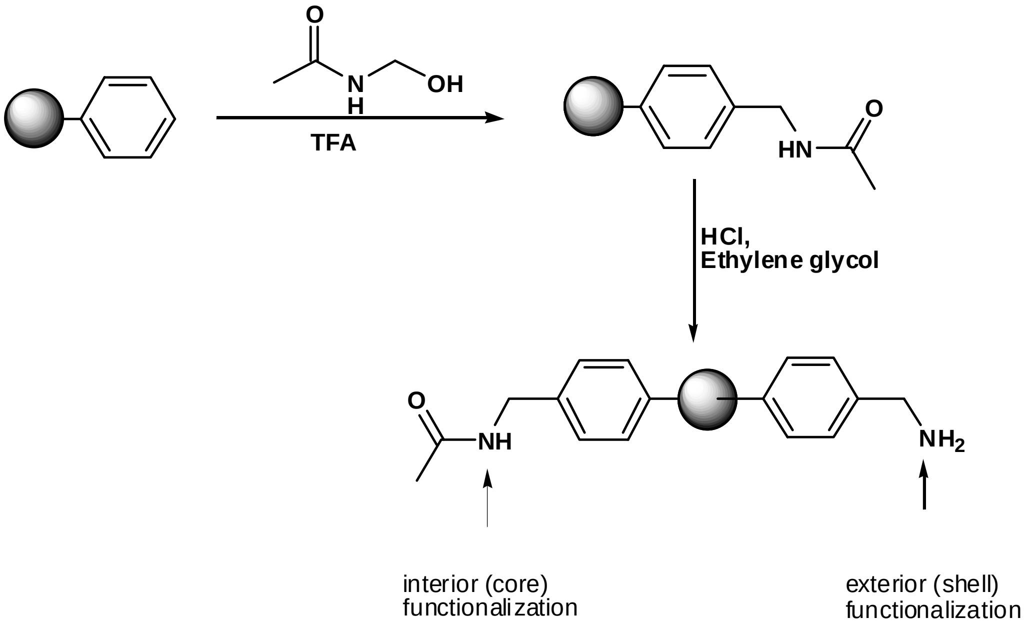
1.2. Polyalkenes

Polyalkene polymers have been the most widely used class of macromolecules in organic synthesis. This is probably due to the combination of their easy synthesis, relative inertness, and low cost. Since heterogeneous divinylbenzene crosslinked polystyrene is widely commercially available in various forms, such as lightly cross-linked and swelling microporous resin and highly cross-linked and nonswelling macroporous resin varieties, and derivatized with many different functional groups, it has probably been used more often than any other polymer in the context of organic synthesis. However, recent years have seen the use of new variations of polystyrene as well as other polyalkenes, such as polyisobutylene, polynorbornene, poly(styrene-*co*-maleic anhydride), and polyacrylamides.

1.2.1. Polystyrene

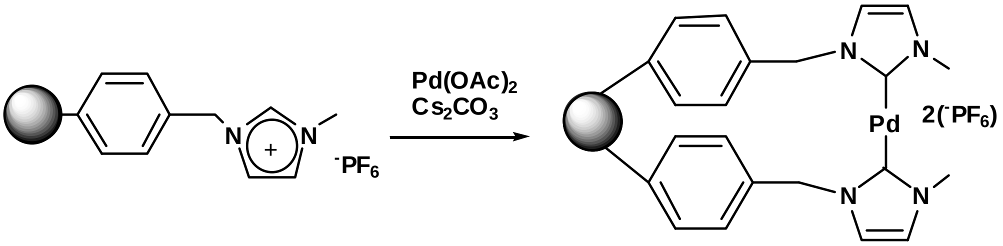
To improve the performance of polystyrene in organic synthesis applications, several strategies have been examined (1) using heterogeneous cross-linked polystyrene in different formats or preparing the polymer in such a way that the functional groups are concentrated toward the surface of the resin, (2) using a cross-linker other than divinylbenzene to heterogenize polystyrene in order to modulate the physical and chemical properties of the resin, (3) adding functional groups to the polystyrene backbone that provide desired properties, and (4) grafting polystyrene onto a heterogeneous support and the use of the graft as the point of substrate/reagent/catalyst attachment to reduce the importance of resin swelling.

As mentioned previously, one of the primary concerns when using a heterogeneous polymer such as Merrifield resin in organic synthesis is the ability of the resin to absorb the reaction solvent and swell. This is due to the fact that the polymers are generally randomly functionalized and that the majority of the functional groups are located on the interior of the bead. If the solvent cannot access these sites, neither can the dissolved reagents, catalysts, or substrates with which they are meant to react. Lee has addressed this issue by developing a new method for functionalizing crosslinked polystyrene beads in such a way that the majority of the resulting functional groups are located close to the exterior of the beads. He refers to such materials as core-shell resins, where the core is relatively unfunctionalized and the shell is highly derivatized. An aminomethyl polystyrene resin was the first reported example of this concept and was prepared from commercially available preformed polystyrene beads by aminomethylation to form protected core-shell aminomethyl functionalized heterogeneous polystyrene,[35,36] followed by the use of the polar solvent ethylene glycol in the amine deprotection step. Since the polystyrene resin did not swell in the solvent, only the amine groups close to the surface of the bead were deprotected during the synthesis.



Scheme 1: Synthesis of Core-Shell Aminomethyl Functionalized Heterogeneous Polystyrene

It should be emphasized that since only the exterior portion the beads are functionalized with amine groups, the loading level of resins prepared in this way must be lower than that for resin beads of the same size that possess the desired functionalization throughout their interiors. Lee reported another method for ensuring that the functional groups, in this case *N*-heterocyclic carbene (NHC) ligands, were located in the shell of a resin bead, thereby reducing the need for resin swelling. In this case, the monomer, which is immiscible in both the styrene and aqueous phases of a suspension polymerization reaction, was used.[37] It was found that the ionic liquid nature of monomer allowed it to be located at the interface between the two phases during polymerization, and therefore, the NHC groups were incorporated on the surface of support as the beads were formed. Palladium was attached to the heterogeneous NHC functionalized polymer, and it was used effectively to catalyze Suzuki,[11,38] Heck,[39] and Sonogashira[40] reactions in which DMF or a DMF/water mixture was used as the reaction solvent.



Scheme 2: Synthesis of Core Shell NHC functionalized Heterogeneous Polystyrene

Hawker and Fre´chet reported the complimentary approach of concentrating the functional groups attached to a polystyrene in the interior of a soluble star polymer matrix so that the catalytic groups are core-confined due to the use of low molecular weight macro initiators that form the surface of the final polymer.[41] This technique allows for the simultaneous use of basically incompatible reagents, such as acids and bases, since they are physically isolated from one another. For example, such core-functionalized star polymers could be prepared by reacting polymer with monomer, which is a derivative of sulphonic acid, and divinylbenzene to form sulfonic acid core functionalized star polymer, or by reacting polymer with monomer, which is a derivative of pyridine, and divinylbenzene to afford 4-(dialkylamino) pyridine core functionalized polymer. It was found that these acid and base functionalized polymers can be used together in a one-pot acetal hydrolysis/ Morita-Baylis-Hillman reaction sequence with substrates to efficiently form hydrolysed product. They applied the same concept to an iminium/enamine reaction cascade where the use of two differently functionalized star polymers allowed the simultaneous use of four catalysts that normally could not all exist together.[42]

It was seen that, when the cross-linker was based on an oligo(ethylene glycol) group, the polymer became more compatible with polar solvents and can function better as a support for solid-phase peptide synthesis than does Merrifield resin.[43] In contrast to most of the early research in this area that centered on the use of highly polar oligo(ethylene glycol) groups to cross-link polystyrene to prepare polymer supports for peptide synthesis, Janda used polytetrahydrofuran-based cross-linkers in the suspension polymerization of styrene to prepare polymers for general organic synthesis.[44,45] The inspiration behind this concept was the maxim “like dissolves like” and that since THF is a good solvent for many organic reactions, incorporating a related polyether into a polystyrene resin should increase polymer swelling in this solvent. Somewhat surprisingly, it was observed that the swelling of resins prepared with such cross-linkers in THF was universally greater than that for analogous divinylbenzene cross-linked polymers and virtually independent of the length or structure of the polytetrahydrofuran cross-linker. These polytetrahydrofuran-based cross-linkers of polystyrene, which could be easily prepared in one pot on a large scale from inexpensive commercially available starting materials, was settled on for the preparation of what is now known as JandaJel.[46]

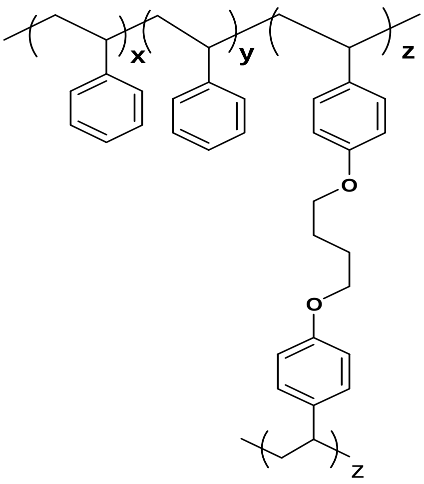


Figure 4: JandaJel

This polymer has been prepared with pendant arsines,[47,48] phosphines,[49] and other reagents,[50,51] using functionalized styrene monomers in the suspension polymerization reaction, and in all cases, the supported reagents showed good swelling in the solvents in which they were used. Interestingly, JandaJel was used for the solid-phase synthesis of the classically difficult to synthesize ACP(65- 74) peptide sequence, with better results in terms of overall yield and product purity than was achieved using Merrifield resin.[52] Solid-phase synthesis of small organic molecules, which can be used as drug, is also efficient using JandaJel as the support,[53,54] and as an illustration of the value of the large degree of swelling that JandaJel exhibits, it was successfully used in multipolymer reactions where a separate homogeneous polymer-supported reagent was reacted with it.[55] In one such example, JandaJel functionalized with phosphine groups was able to react with a separate soluble polymer-supported azo reagent to effect Mitsunobu reactions, whereas a divinylbenzene cross-linked polystyrene-supported phosphine reagent was unreactive.[56]

Kobayashi has extended his research regarding the microencapsulation of metal catalysts in polystyrene and developed the concept as polymer incarceration, using oligo(ethylene glycol) groups to cross-link polystyrene. For example, copolymerization of styrene, with derivatives of ethylene glycol afforded cross-linked polymer, which was used to generate one of the first examples of an incarcerated palladium catalyst.[57] The details of the cross-linking reaction have not been reported and a proposed structure for the obtained cross-linked polymer has never been published in the chemical literature. Regardless of the ambiguity surrounding the cross-linking in these materials, numerous polymer incarcerated metal catalysts have been used with excellent results in a broad range of reactions and are highly reusable. The initial reports involved the entrapping of palladium to generate catalysts, in the reactions of alkene hydrogenation and allylation using allylic carbonates.[57,58] These catalysts were subsequently used in Suzuki-Miyaura,[35,36] Heck,[60,61] aminocarbonylation,[62] and amidation[63] reactions. Polymer incarcerated scandium triflate,[64] ruthenium,[65] platinum,[66] and gold[67] catalysts have also been reported and used to perform Mukaiyama aldol, alcohol, and sulfide oxidation, hydrogenation, and indole synthesis reactions, respectively. Significantly, in all reported applications of these polymer incarcerated metal catalysts, no significant metal leaching into the desired synthesis product was observed. Thus, they should be useful in synthetic applications where this issue is a concern, such as pharmaceutical manufacturing. Incarceration in the heterogeneous polymer rendered the enzyme easily recyclable without attenuating its natural enantioselectivity. Variations of this microencapsulated palladium catalyst are now commonly referred to as Pd-EnCat and have been used in a large number of variations of Suzuki- Miyaura[68,69] and hydrogenation[70] reactions from which the catalyst could be recovered and reused with no appreciable decrease in catalytic efficiency, in some cases up to ten times. Additionally, an analogous microencapsulated osmium tetroxide catalyst has been reported for use in alkene dihydroxylation reactions.[71] The porosity of such polymer encapsulated catalysts has been studied,[72] and Jones has used Pd-EnCat together with poly(4-vinylpyridine) to suggest that when this catalyst is used in Heck reactions, catalysis occurs outside the polyurea matrix by a soluble palladium species.[73] Chiral cross-linkers have also been used to prepare heterogeneous polystyrene resins where the chiral moiety is used as a ligand in asymmetric catalysis. Hoveyda and Schrock have used polymer cross-linked with chiral monomer to prepare a recyclable chiral molybdenum olefin metathesis catalyst that was used in enantioselective ring-opening and ring-closing metathesis reactions where the products were isolated with only slightly lower enantiomeric excess than when the corresponding small molecule catalyst was used.[74] Similarly, Seebach has used tetraaryl chiral ligand as cross-linkers, to prepare a variety of polystyrene beads with embedded α,α,α,α-tetraaryl-l,3-dioxolane-4,5-dimethanol (TADDOL) groups that were used to prepare recyclable chiral titanium Lewis acid catalysts for addition of Bu_2Zn to PhCHO.[75]

The PEG derivatives of cross-linked polystyrene performed well in solid-phase peptide synthesis, probably due to their good swelling in the required solvents. Motivating from these results, Bradley developed a complimentary strategy and added short oligo(ethylene glycol) groups to the backbone of divinylbenzene cross-linked polystyrene to make the resin beads more compatible with polar solvents.[76] The key difference between this strategy and Bayer's design of PEG-based Tentagel is that, in the latter, the PEG groups act as spacers to separate the polystyrene backbone from the point of synthesis, whereas, in the former, the PEG groups are simply spectators added to modulate the physical properties of the polymer. Toy later reported results similar to Bradly's in a study of polymer-supported phosphine catalysts for

Morita- Baylis-Hillman (MBH) reactions.[77] Interestingly, incorporation of hydroxyl groups into the polymer using suitable monomer resulted in a resin that did not swell appreciably in THF but that was still a modestly effective catalyst. More recently, Bergbreiter has shown that poly(4-*tert*butylstyrene) is hydrophobic enough to be selectively soluble in a nonpolar organic solvent so that its quantitative removal was achievable using biphasic polar liquid/nonpolar liquid separation.[78] Plenio almost simultaneously reported a similar strategy using poly(4-methylstyrene) to support phosphine ligands for use in palladium catalyzed Sonogashira and Suzuki coupling reactions.[79] This polymer was used in a cyclohexane/DMSO solvent mixture for the former and a cyclohexane/nitromethane solvent mixture for the latter. In a subsequent publication this polymer was applied in a continuous Sonogashira reaction process in a fixed bed reactor.[80] Passing the polar substrate containing DMSO phase through the nonpolar catalyst containing cyclohexane or heptane phase led to virtually quantitative conversion for the coupling of various aryl bromides with phenylacetylene.

Bayer grafted PEG onto heterogeneous polystyrene resin in order to move the point of peptide synthesis away from the interior of the beads and reduce the need for resin swelling. The first example was reported by Zhao and involved the radiolytic grafting of polystyrene onto the surface of fluoropolymer tubes.[81] This was accomplished by immersing the tubes in a styrene, MeOH, and H_2SO_4 mixture and then γ-irradiating with a Co-60 source. The polystyrene grafts thus formed on the tubes were then aminomethylated and used as surfaces for solid phase nitrile oxide and Diels-Alder cycloaddition reactions. Hodges later reported the use of living free radical polymerization to graft polystyrene onto heterogeneous polystyrene resin to form what he referred to as Rasta resin.[82] This methodology was reported to be useful for the addition of grafts functionalized by electrophilic groups that might be incompatible with conventional suspension polymerization techniques. More recently it was found that grafted resins could be prepared efficiently using microwave initiated polymerization,[83,84] and Fontaine has extended this concept by using atom transfer radical polymerization (ATRP) initiators to attach poly(2- vinyl-4,4-dimethyl-5- oxazoline) grafts that are efficient at nucleophile scavenging[85] or that can serve as the platform for a densely functionalized basic amine resin.[86]

1.2.2. Polyisobutylene

This polymer is a terminal alkene that is commercially available with an average molecular weight of 1000 or 2300 Da. It is reported that a major advantage of polyisobutylene over previously studied terminally functionalized polyethylene is that the former is readily soluble in a variety of nonpolar solvents whereas the latter is only soluble in such solvents at >75 °C.[12,78,87]

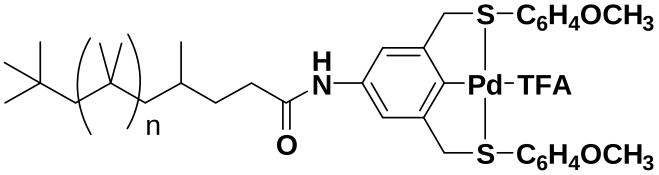


Figure 5: Terminally functionalized polyisobutylene-supported catalyst

Similar to the previously mentioned poly(4-*tert*-butylstyrene), polyisobutylene is very selectively soluble in nonpolar solvents such as heptane. Its carbon-carbon double bond can be transformed by the standard reactions of alkenes into more useful groups for attaching catalyst or reagent groups, such as hydroboration to form a primary alcohol. This alcohol can then be converted to a mesylate group, which can be displaced by a range of nucleophiles for example, carboxylic acid and phosphine.[87,88] The first reported use of polyisobutylene as a catalyst support involved anchoring a sulfur-carbon-sulfur Pd(II) species to polymer functionalized with mesylate group. The resulting catalyst was used to perform Heck, Sonogashira, and allylic substitution reactions with good recyclability.[87] More recently polyisobutylene has been used to support chiral bisoxazoline ligands for copper catalyzed cyclopropanation reactions,[89] as well as to serve as the basis for a self-separating atom transfer radical polymerization catalyst.[90] A polyisobutylene-supported RCM catalyst[91] and a chromium-based polycarbonate polymerization catalyst have also been reported.[92] All of these supported catalysts exhibited similar activity to their unanchored counterparts, and they were easily recovered and reused without appreciable loss of activity.

1.2.3. Polynorbornenes

The use of ring-opening metathesis polymerization (ROMP) to prepare polynorbornene derivatives amenable for use in synthesis has been widely studied. The main motivations for using such polymers are that ROMP is generally compatible with many functional groups, and with proper monomer design, the polymers can be very densely functionalized. Much of the early work in applying polynorbornenes has been reviewed by both of the pioneers in this field, Barrett[93] and Hanson.[94] Early on, Barrett referred to polynorbornenes, both with or without a norbornene-based cross-linker, as ROMPgel[95] and polystyrene resin grafted with polynorbornene as ROMPsphere[96].

Figure 6: ROMPgel (1) and ROMPsphere (2)

Janda reported the methodology of suspension polymerization to synthesise crosslinked ROMPgels in spherical beads.[97] Using this methodology a large number of norbossrnene-based cross-linkers could be used to prepare

ROMPgels as heterogeneous resin beads. Recent applications of polynorbornenes as a reagent support include the report by Toy and Hanson that a combination of non-cross-linked ROMPgels functionalized with phosphine groups and diethyl azodicarboxylate can react together in two-polymer Mitsunobu reaction in which the desired product was isolated in a highly pure state after filtration to remove all the polymeric materials.[56] Other reports regarding the development and use of ROMPgels include the synthesis of a bifunctional version for the immobilization of Wilkinson's catalyst.[98] For this, Barrett copolymerized a phosphine monomer together with imidazolium hexafluorophosphate monomer and a norbornene-based cross-linker to form bifunctional ROMPgel. Heating the resultant polymer in the presence of Wilkinson's catalyst allowed for immobilization of the metal through a ligand displacement process to form the desired supported catalyst. The role of the imidazolium hexafluorophosphate groups in this catalyst is not clear, but good results were obtained in a series of parallel hydrogenation reactions. This concept of using two different functionalized monomers in the polymerization reaction was extended to the copolymerization of hydroxyl substituted monomers and norbornene-based cross-linker to form polar diol containing ROMPgel that, due to the presence of the hydroxyl groups, exhibited excellent swelling in polar solvents such as methanol.[99] ROMPgel containing polar diols was effective in the transformation of a series of aldehydes into the corresponding alkynes in methanol. In addition to the ROMPgel and ROMPsphere formats described above, polynorbornene has also been prepared in monolithic form by Buchmeiser for use as a catalyst support. The monolithic support was prepared by copolymerization of norbornene and norbornene based cross-linker in the presence of CH_2Cl_2 and 2-propanol within a borosilicate column using $Cl_2Ru(PCy_3)$-(CHPh) as the ROMP catalyst.[100] Functionalization of the thus formed polymer monolith with a ligand group bearing norbornene monomer was followed by capping with ethyl vinyl ether, carbene generation with DMAP, and metal can be loaded to it. The combination of good and poor solvents used in the polymerization process ensured formation of the desired monolith microstructure with sufficient macroporosity. The metal functionalized polynorbornene was found to be highly active in flow-through ROMP and RCM reactions, leading to metal free products. Using the same polynorbornene structure and catalyst immobilization strategy, supported modified Grubbs-Hoveyda catalysts[101,102] chiral Schrock catalyst,[103] and Grubbs-type catalyst[104] have also been developed and successfully employed in plentiful metathesis reactions. Monoliths prepared by copolymerization of norbornene with norbornene-based cross-linker have also been reported that were fuctionalized as Pd catalyst for Heck reactions[105] and as Grubbs-Hermann type metathesis catalyst.[106] Other recent applications of polynorbornene supports include Barrett's use of ROMPgel to support a thiazolium organic catalyst for use in Stetter reactions,[107] and both ROMPgel and ROMPsphere have served as platforms for coupling reagents used in peptide synthesis[108] and a photooxygenation catalyst.[109] Hanson has reported ROMPgel functionalized with phosphonyl dichloride groups for amine scavenging[110] and monoamine hydrochloride groups for scavenging electrophiles.[111] ROMPgel was also used to support benzenesulfonyl azide groups used in diazo-transfer reactions,[112] benzylsulfonium salts in benzylation reactions,[113] carbodiimide groups for coupling reactions,[114] phosphine groups for cross-coupling reactions,[115] TEMPO in alcohol oxidation reactions,[116] pincer Pd(II) complexes as precatalysts in Heck reactions,[117,118] and salen complexes for a variety of applications.[119-121] Most recently, Polo has used the ROMPgel norbornene monomer framework to display 2 cyclopentadiene or indene groups in the proper orientation for use as zirconium “self-immobilizing” precatalysts.[122] Exposure of the prepared biscyclopentadienyl and bisindenyl zirconocenes to methylaluminoxane resulted in the expected polymerization to form immobilized catalysts that could be reactivated and used effectively in ethylene polymerization. Nomura has shown that monofunctionalized polynorbornene can serve as a phase tag, since it precipitates in methanol.[123,124] For example, polynorbornene terminally functionalized with various pyridine groups can be used as a ligand in hydrogenation reaction. Upon completion of the reaction, methanol can be added to precipitate the polymer-metal complex for easy separation and reuse.

1.2.4. Poly (styrene-*co*-maleic anhydride)

The alternating copolymer of styrene and maleic anhydride can be precipitated from hexanes and is commercially available with an average molecular weight of approximately 550000 Da, containing 10-15% monomethyl ester. The high concentration and reactivity of the cyclic anhydride groups of this polymer make it ideal for use as a reagent support. Najera first reported treatment of this polymer with hydroxylamine to afford polymer-supported *N*-hydroxysuccinimide for use in peptide coupling reactions that exhibited very low levels of racemization.[125] At the end of the reactions hexane was added so that the polymeric material could be removed by filtration. Polymer-supported *N*-hydroxysuccinimide was then treated with either 9-fluorenylmethoxycarbonyl chloride (Fmoc-Cl)[126] or (2,7-di-*tert*-butyl-9-fluorenyl)methyl chloroformate (Bts-Fmoc-Cl)[127] to form corresponding reagents, that were useful for amino acid protection. Alternatively, supported *N*-hydroxysuccinimide could be reacted with allyl chloroformate (Alloc-Cl) or propargyl chloroformate (Proc-Cl) to form the corresponding amino group protecting reagents.[128] On the other hand, supported *N*-hydroxysuccinimide could be reacted with ammonia or a primary amine to form ammonium salts, which can react with a carboxylic acid in the presence of a coupling reagent to form amides[129] or functionalized as a uranium salt for use as polymer-supported peptide coupling reagent.[130] In order to showcase the utility of the polymer in nonpeptide synthesis applications, Najera reacted poly(styrene-*alt*-maleic anhydride) with di(2-pyridyl)methylamine in order to generate recoverable palladium catalyst for cross-coupling reactions that could take place in water.[131]

1.2.5. Poly (acrylic acid) Derivatives

Bergbreiter grafted poly(acrylic acid) onto both polyethylene and polystyrene. Hydrolysis of polymer supported acrylate resulted in poly(acrylic acid) functionalized polymer, which can be used to immobilize Pd(II) as a catalyst for hydrogenation reactions. Pd (II) in the immobilized catalyst can be reduced with H_2 to form Pd (0), which was an active catalyst for allylic substitution and Heck reactions.[132]

Several polyacrylates have been reported as soluble supports for homogeneous catalysts where the ester groups are used to control the solubility of the polymer. Bergbreiter reported the use of a fluoroacrylate monomer to prepare polyacrylates selectively soluble in fluorous solvents using a mixture of ester monomers to synthesize copolymers.[133] Reaction of these ester functionalized polymer with a primary amine afforded phosphine functionalized polymer, which was in turn converted into hydrogenation catalyst by the rhodium metal ion incorporation using corresponding salts. The fluorous nature of rhodium functionalized catalyst allowed it to be readily recovered from alkene hydrogenation reactions and reused without loss of activity by liquid/liquid separation. Akgerman and Fackler have further thoroughly studied this catalyst in a variety of hydrogenation and hydroformylation reactions under several conditions,[134] and Yao has reported a catalyst for RCM based on the same fluorous polyacrylate polymer.[135] Wills later described a similar strategy using methyl methacrylate and an ethyl PEG ester methacrylate to synthesize polymer-supported hydrogenation catalysts, which were soluble in organic solvents and used as ligands for asymmetric transfer hydrogenation reactions.[136] Buchmeiser has reported poly(methacrylate)-based polymer monoliths synthesized by copolymerizing ethyl methacrylate and acrylate based cross-linker.[137] This was followed by the generation of the corresponding carbenes, and subsequent copper immobilization afforded lightly loaded supported Cu(I)-NHC complexes, approximately 20-25 μmol Cu g^{-1} each, which were used to catalyze arylaldehyde cyanosilylation and hydrosilylation reactions in a continuous flow setup.

Bergbreiter comprehensively studied the use of poly(*N*-isopropylacrylamide) (PNIPAM) as a support in organic synthesis,[30,31,138] In reactions using any of the palladium immobilized polyacrylamide catalysts, the products are separated from the catalyst by a liquid/liquid biphasic separation with the catalyst containing liquid phase ready for direct reuse. Ikegami reported addition of ammonium groups to PNIPAM to generate a polymer that could be used to immobilize phosphotungstic acid and it was used effectively as a heterogeneous catalyst for allylic alcohol, amine, and sulfide oxidation with hydrogen peroxide as the penultimate oxidant.[139] Janda has reported the synthesis of a poly(*N*,*N*-dimethyl acrylamide) cross-linked hydrogel.[140] This polymer was found to be useful as a water compatible anchor for the photosensitizer hematoporphyrin.[141] An aqueous suspension of the photosensitizer attached polymer on exposure to light, efficiently generated singlet oxygen for reaction with anthracene. Biffis subsequently described the use of a related polyacrylamide in microgel form that was soluble in a range of organic solvents to stabilize metal nanoclusters.[142,143] The nanoclusters of palladium, platinum, and gold that were studied as catalysts in aerobic alcohol oxidation reactions.

Several other polyalkenes have been used as supports for catalysts. Beletskaya has shown that poly (*N*-vinylimidazole) can be used as a recyclable catalyst for the addition of thiols to Michael acceptors in water/ethanol solvent mixtures.[144] This application can be viewed as a pre-functionalized polyethylene derivative with pendant imidazole groups. Beletskaya has also reported the synthesis of poly (*N*-vinylimidazole-*co*-*N*-vinylcaprolactam) and the use of both poly (*N*-vinylimidazole) and poly (*N*-vinylimidazole-*co*-*N*-vinylcaprolactam) to immobilize palladium for Heck reaction catalysis.[145] Such reactions were found to be more efficient with poly (*N*-vinylimidazole-*co*-*N*-vinylcaprolactam) than with poly (*N*-vinylimidazole). Additionally, Vankelecom reported the use of ionic poly(diallyldimethylammonium chloride) in a method for supporting both an ionic liquid and Wilkinson's catalyst in hydrogenation reactions,[146] and Jones and Weck have used linear ring-opened polycyclooctene, as well as some cyclic oligomeric analogues, to support a cobalt-Salen complex, as well as some cyclic oligomeric analogues, for epoxide kinetic resolution reactions.[147]

1.3. Polyethers

1.3.1. Poly (ethylene glycol)

PEG is a water soluble linear polymer that is also compatible with a variety of polar organic solvents and can be precipitated from either 2-propanol or diethyl ether.[32,33] Now a days, this composite polystyrene-PEG material comes in many forms from a variety of dealers with various trade names.[148-150] Lee has used a variation of his core-shell polymer synthesis concept to prepare PEG grafted polystyrene by using Jeffamine derived macromonomer.[151,152]

However, polystyrene grafted with PEG is still probably best known as Tentagel, and it remains widely used for solid-phase synthesis.[27,28] More recently, the water compatibility of PEG-based Tentagel has been exploited and it has been used as a heterogeneous support for metal catalysts applied in aqueous media. Uozumi has pioneered much of this work and used Tentagel as a support for a variety of palladium catalysts. A combinatorial library of Tentagel-supported chiral phosphine- palladium complexes with amino acid spacers between the PEG chain and the phosphine group has also been studied in allylic substitution reactions.[153] Tentagel has also recently been used to support palladium nanoparticles for aqueous applications.[154] Fre´chet used methacrylate esters of ethylene glycol oligomers in a suspension polymerization process with ethylene glycol based cross-linker to synthesize hydroxyl group functionalized beads that swell well in a variety of polar solvents that had relatively high loading values (1.2-1.8 mmol g^{-1}).[155] Recently, Zhu has used epichlorohydrin cross-linked poly(vinyl alcohol) beads prepared by a reverse suspension polymerization process,[156,157] which themselves have utility in organic synthesis,[158] as the starting material for anionic grafting of PEG in order to prepare a resin with higher loading than typical PEG-based Tentagel.[159] Meldal has had a continuing interest in preparing resins for solid-phase organic chemistry that are composed almost entirely of PEG and has reported what are known as PEOPOP, SPOCC, and POEPS-3 resins with PEG components of various molecular weights.[160] These resins all exhibit good mechanical properties, excellent swelling in polar solvents and high loading capacity of 0.9-1.2 mmol g^{-1} that can be used in a variety of solid-phase synthesis applications[161] and, interestingly, even as a functionalizable optical fiber cladding material.[162] Albericio has described the use of ChemMatrix resin that is cross-linked by PEG as a support for solid-phase peptide synthesis.[163] This polymer is notable in that it only contains primary ether bonds and is therefore highly chemically stable. Amazingly, when it was used as the support for the linear solid-phase synthesis of the β-amyloid (1-42) peptide sequence, the crude product was obtained with 91% purity. It is proposed that the great efficacy of the resin is due to its ability to prevent peptide aggregation.

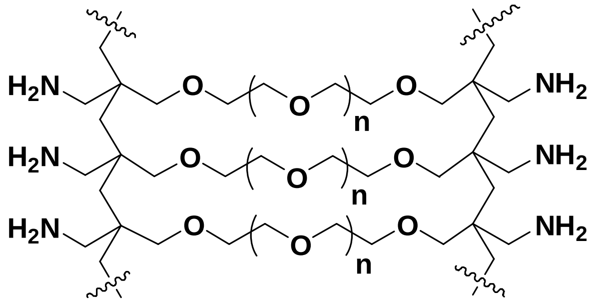


Figure 7: ChemMatrix

1.3.2. Polyglycerol

One of the major disadvantages of PEG as a support for organic chemistry is that it can only be terminally functionalized and hence its loading level is inversely proportional to its molecular weight. To overcome this limitation while maintaining the general polyether structure of PEG, polyglycerol has been subjected to study. Reaction of an alcohol with a base and excess glycidol results in ring-opening polymerization to form a soluble, hyperbranched polymer with both primary and secondary alcohol groups on the periphery.[164,165] The physical properties of numerous polyglycerol derivatives have been extensively studied,[166] and they have been found to be biocompatible in numerous life science applications.[167] In the context of organic chemistry, polyglycerol has been used both as a synthesis platform and as a support for reagents and catalysts. A multistep synthesis of a series of γ-aminobutyric acid lactam analogues using polyglycerol with a molecular weight of 8000 Da and a hydroxyl group loading level of 13.5 mmol g^{-1} as the support was reported.[168]

At the end of each synthetic reaction, the polymer-supported product was isolated by dialysis with an appropriate membrane. In terms of using polyglycerol as a reagent support, a procedure for the conversion of hydroxyl groups of polyglycerol into morpholine groups has been reported.[169] On the other hand; the hydroxyl groups can be used to immobilize boronic acids for use in Suzuki-Miyaura reactions.[170] In this application, product purification was achieved by precipitation and ultrafiltration. Similar to the report by Toy and Hanson regarding the simultaneous use of 2 polynorbornene-supported reagents for performing Mitsunobu reactions, Haag has shown that polyglycerol supported phosphine and azo reagents can also be used for this purpose.[171] Most significantly, Haag and Liese have shown that polyglycerol-supported Salen complexes of chromium and manganese can be used in a membrane reactor for homogeneous asymmetric catalysis of Diels-Alder,[172] epoxidation,[173] and epoxide kinetic resolution reactions.[174] In order to simplify and speed up polymer separation, polyglycerol has been grafted onto polystyrene resin to form a heterogeneous support using a heterogeneous alcohol core.[175] Polystyrene-*graft*- polyglycerol has similar properties to Tentagel in terms of swelling, but has the key advantage of having a much higher loading capacity, up to 4.3 mmol g^{-1}.

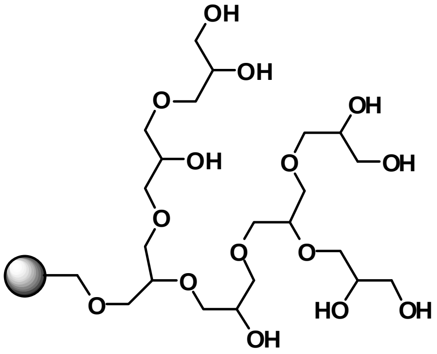


Figure 8: Heterogeneous polystyrene supported Polyglycidol

Steinke reported a non-PEG polyether resin with the name SLURPS (superior liquid uptake resin for polymer-supported synthesis).[176] The starting material for SLURPS is 1,4-butanediol derivative, and while its preparation is based on polymerization of mixtures of enol ether monomers, and it had a polyether structure. Conversion of the acetate groups to bromides allowed for installation of various linker groups so that solid-phase peptide synthesis could be performed.[177] Janda has reported an analogue of Tentagel where the PEG grafts are replaced by polytetrahydrofuran.[178] The utility of this new resin type was established by the solid-phase synthesis of 3-methyl-1-phenyl-2-pyrazolin-5-one using standard acylation, and imine formation reactions.

1.4. Poly(ethylene imine)

Rademann reported a completely different strategy for the generation of solid phase synthesis resins with very high loading levels based on a polyamine structure.[179] Commercially, poly(ethylene imine) was condensed with small quantities of terephthalic dialdehyde to form a cross-linked polyimine network. The imine groups were subsequently reduced to produce poly(ethylene imine)-based ULTRA resin, in which all of the secondary amine nitrogen atoms were available for derivatization and a loading level up to 14.0 mmol g^{-1} was achieved and it was used in peptide and organic synthesis. Meldal first reported the reaction between poly(ethylene imine) with acryloyl chloride that was polymerized using the inverse suspension polymerization technique to form polymers which were referred to as ULTRAMINE resin.[180]

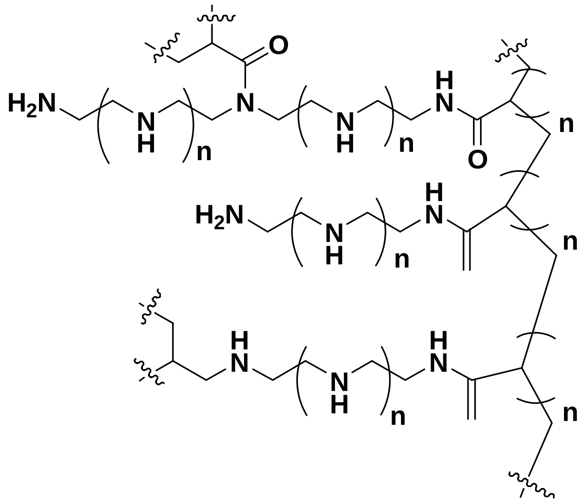


Figure 9: ULTRAMINE Resin

Since some of the macromonomers contained multiple acrylamide groups, the resulting polymers were cross-linked and heterogeneous. Furthermore the amine group concentration could be increased by complete reduction of the amide groups of ULTRAMINE resin so that the resulting resin could function as an acid scavenger. Neumann reported the use of poly(ethylene imine) alkylated with iodomethane and 1-iodododecane to immobilize polyanionic polyoxometalates to form a catalyst for aqueous oxidation reactions using H_2O_2,[181] which was apparently similar to the approach of Ikegami.[139]

1.5. Poly (2-oxazoline)

A group of amphiphilic polymers for making use as supports in organic synthesis that was prepared by cationic polymerization of 2-oxazoline monomers was reported by Weberskirch.[182]

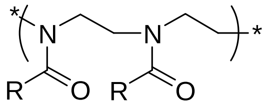


Figure 10: Polyoxazoline

The living nature of the polymerization process allowed for part copolymers to be synthesized in which one block was water compatible and the other part was hydrophobic. The first example of such a polymer contained 2,2′-bipyridine groups in the hydrophobic portion and was useful as a macroligand in the atom-transfer radical polymerization of methyl methacrylate in water.[182] Subsequent products contained pendant carboxylic acid groups that could be functionalized with a chiral phosphine group for use in aqueous asymmetric hydrogenation reactions,[183] Hoveyda-Grubbs-type catalyst for RCM in water,[184] a rhodium carbene complex for aqueous two-phase hydroformylation reaction,[185] or a chiral cobalt-salen complex for hydrolytic kinetic resolution reactions.[186] Furthermore, other variations of this theme include a related polymer-supported palladium carbene complex for coupling reactions in water[187,188] and a triphenylphosphine for aqueous two-phase hydroformylation reactions.[189]

1.6. Poly (xylylviologen dibromide)

Poly(xylylviologen dibromide) (figure 11) has been known for several years,[190] but only recently has Uozumi shown that it can be used to support palladium nanoparticles.[191] These heterogeneous palladium nano particles were used to catalyze R-alkylation of ketones with primary alcohols, and ring opening alkylation of cyclic 1,3-diketones with primary alcohols,[192] and was readily recycled. A related supported phosphotungstate catalyst has also been reported.[193]

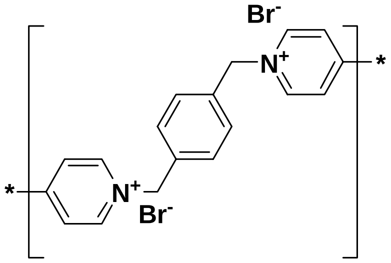


Figure 11: Poly(xylylviologen dibromide)

1.7. Silicon polymers

After oxygen, silicon is the second most abundant element of the Earth's crust. Silicon, among the elements, is most unique in its ability to homocatenate and form stable long chains in a manner similar to carbon. Silicon polymers include polysiloxanes, polysilanes and polycarbosilanes. Polysiloxanes and polysilanes are coming under the category of inorganic polymers. Polycarbosilanes (PCS)[194,195] are rather neglected class of polymers; this class of polymers can be compared to the existing classes of inorganic and organic polymers, they possess a combination of low t_g's and high synthetic versatility similar to polyphosphazenes and polysiloxanes and with good chemical backbone stability similar to that of polyolefines.[196] Polycarbosilanes can represent structural hybrid between polysilanes and polyolefines, which have found applications as liquid crystals,[197-199] SiC-precursor[200-202] and catalyst[203,204]; recently considerable interest has been focused on it.

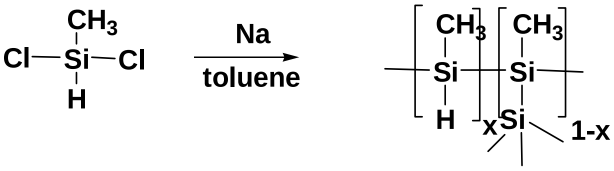
1.7.1. Polysilanes

Polysilanes[205] are polymers having silicon backbone with organic substituents and show extraordinary electronic and photophysical properties such as UV absorption,[206] thermochromism,[207] solvatochromism,[208] and electroluminescence,[207] caused by the delocalization of the σ-electrons along the Si-chain. Because of these unique characteristics, polysilanes have attracted broad attention in academia and industry. They can be used as useful materials in semiconductors, radical photoinitiators, precursors for silicon carbide syntheses, and sensors.[209] Variation of substituents and copolymerization of different dichlorodiorganosilanes $SiCl_2R_2$ offers countless possibilities for tailoring chemical and physical properties, e.g., solubility, morphology, and optical activity.[210-213] Optically active polysilanes can be used for chiroptical switching and memory systems for data storage.[214]

The first polysilane derivatives were reported by Kippin by condensation of diphenyldichlorosilane with sodium metal, the product was infusible and insoluble.[215] Burkhard described the preparation of the simple dialkyl derivatives; poly(dimethyl silane), by similar way. The product obtained was with same nature as that of the former.[216]

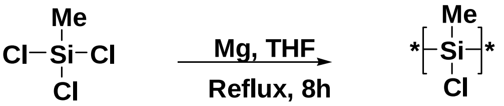
Wesson and William reported the synthesis of soluble homo and copolymers from dimethylsilylene with ethylmethylsilylene or methyl-(n-propyl) silane.[217] West and coworkers described the preparation of soluble polysilane from methylphenyldichlorosilane.

The main synthetic route to polysilanes is by sodium-mediated reductive Wurtz coupling of $SiCl_2R_2$.[218]



Scheme 3: Synthesis of polysilanes by Wurtz type coupling

Silicon polymers resulting from monomers by Wurtz type coupling were insoluble and with highly crosslinked and complicated structures. The synthesis of linear and soluble polysilane, involve the condensation of monomer by Grignard reaction[195].



Scheme 4: Synthesis of polysilanes by Grignard reaction

Usually, functionalization of polysilanes after polymerization process was employed. For example, trimethylammonium moieties bound to phenethyl substituents have been reported by Seki et al.[219] Aromatic hydroxyl functionalities at polysilanes have been introduced by way of trimethoxysilane protected phenols by Horiguchi et al.[220] Möller and co-workers[221] employed polymer modification reactions including hydrosilylation with unsaturated polysilanes with substituents to generate aliphatic hydroxyl substituents.

1.7.2. Polycarbosilane

As polymers that contain both Si and C in their backbone structure, polycarbosilanes have been of primary interest as potential precursors to silicon carbide[222-227], a ceramic material which is of considerable technological importance due to its high thermal, chemical and oxidative stability, as well as for its electrical (semiconductor) and mechanical (high hardness, shock resistance, strength etc) properties. These are not common to any other class of synthetic or natural materials. They also possess extremely high density of molecular functionality at high generations, hence it is not hard to envision a variety of potential application that are opening up for these new polymers in areas such as nanotechnology[228], surface science, bio-medicine, catalysis[203,229], electrochemistry, liquid crystals[197-199], new ceramics materials[200-202], organo-inorganic hybrids and nanocomposites etc. Many of these will clearly play dominant roles in the development of science in the twenty first century, and we have no doubt that silicon will play a prominent role in all of them as well.

First commercial SiC material was introduced by Nippon carbon under the trade name of Nicalon. The synthesis was based on the strategy developed by Yajima and coworkers.[230,231] Early work of Yajima in the 1970s lead to a polycarbosilane with $SiH(CH_3)$ composition, which subsequently found commercial application as a source of SiC fibers. The precursor, polydimethylsilane $[Si(CH_3)_2]_n$, on thermal treatment in an autoclave, was subsequently shown to have a complex structure with extensive branching, along with cyclization and intermolecular Si-Si bonding. Due to its largely insoluble character and lack of functionality appropriate for cross-linking after fiber spinning, processing of SiC fibers typically involved melt spinning followed by thermal treatment in air to get fiber structure. Fig.12 represents the structure of polycarbosilane, which was used as a precursor to SiC.

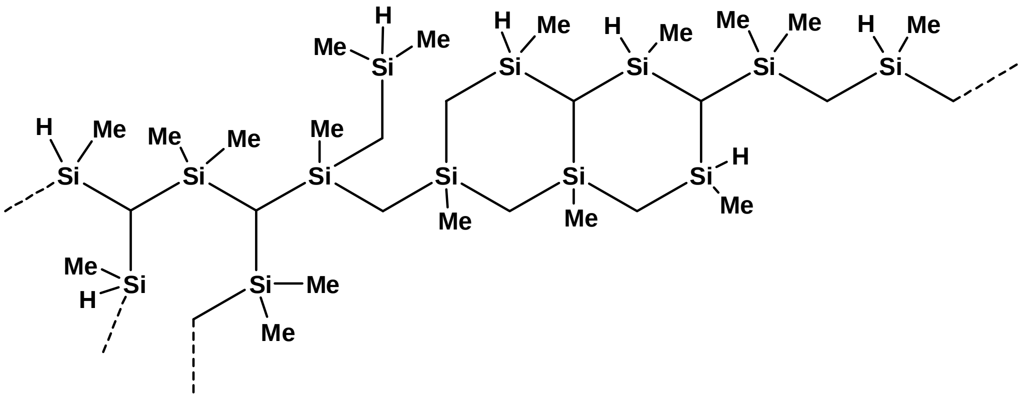


Figure 12: Model structure of Yajima PCS

After the pioneering work of Verbeek[232] and of Yajima the strategy has allowed the production of industrial SiC- based fibers. The main work of Yajima was based on the following transformation.

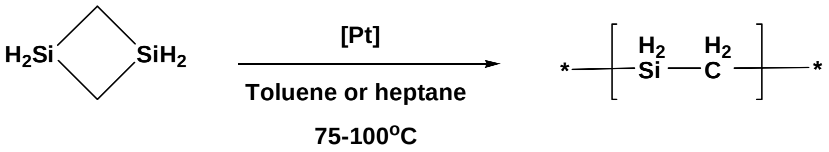
$$\text{Dichlorosilanes} \longrightarrow \underset{\text{PS}}{\text{Polysilanes}} \longrightarrow \underset{\text{PCS}}{\text{Polycarbosilane}} \longrightarrow \text{SiC material}$$

Initially, the monomer used was $(Me_2\text{-}Si)_6$, it was autoclaved at 400°C under inert atmosphere to get the polycarbosilane, the main draw back of this method was the expensive monomer and the use of an autoclave. Later, Yajima proposed a simpler and more economic strategy[233] to synthesise PCS, The chlorosilane monomers on treatment with Na metal will give the polymer, by Wurtz rearrangement. These polysilanes on thermal rearrangement gave polycarbosilanes. The transformation proceeded according to Kumada's rearrangement, i.e. insertion of a methylene group into a Si-Si bond. The PCS obtained by this method was referred to as Mark I. Mark II was introduced by adding small amounts of $(Ph_2Si)_n$ in PDMS or Ph_2SiCl_2 in Me_2SiCl_2, Mark II was found to be having better spinnability than Mark I.[234]

To synthesize polycarbosilanes so many methods are available[203] as thermolysis of polysilanes, ROP reactions, condensation reactions of chlorosilanes are the important methods; the details are listed as follows

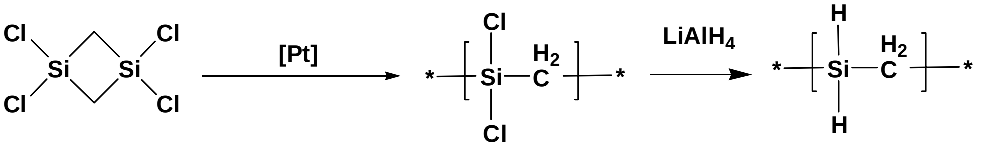
1.7.2.1. Ring opening polymerization reactions

The PCS can be prepared by the ring opening polymerization of 1,3-disilacyclobutane using Pt-group metal derivatives as catalyst. The ring strain might be the driving force of the reaction. Smith claimed the preparation of poly(silylmethylene) by ring opening polymerization of small amounts of 1,3-disilacyclobutane in heptane, using Pt-group metal derivatives as catalyst.[235]



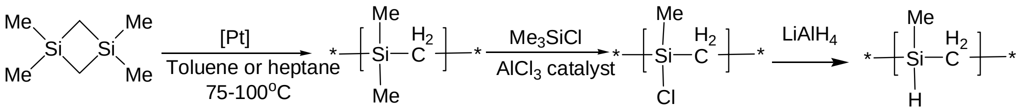
Scheme 5: Synthesis of PCS from 1,3-disilacyclobutane

Wu and Interrante[236] synthesized linear poly(dichlorosilmethylene) *via* ring opening polymerization of 1,1,3,3-tetrachloro-1,3-disilacyclobutane with Pt- catalyst. Direct reduction of this polymer in benzene led to poly(silmethylene) with Mn=12300. The monomer synthesis is tedious. Therefore this method is suitable only for small scale preparation. Analyses were consistent with the expected linear formula. Interrante noted the unusual low crystallization temperature and pointed out the essential role of Si-H bonds in the formation of the network.



Scheme 6: Synthesis of PCS from 1,1,3,3-tetrachloro-1,3-disilacyclobutane

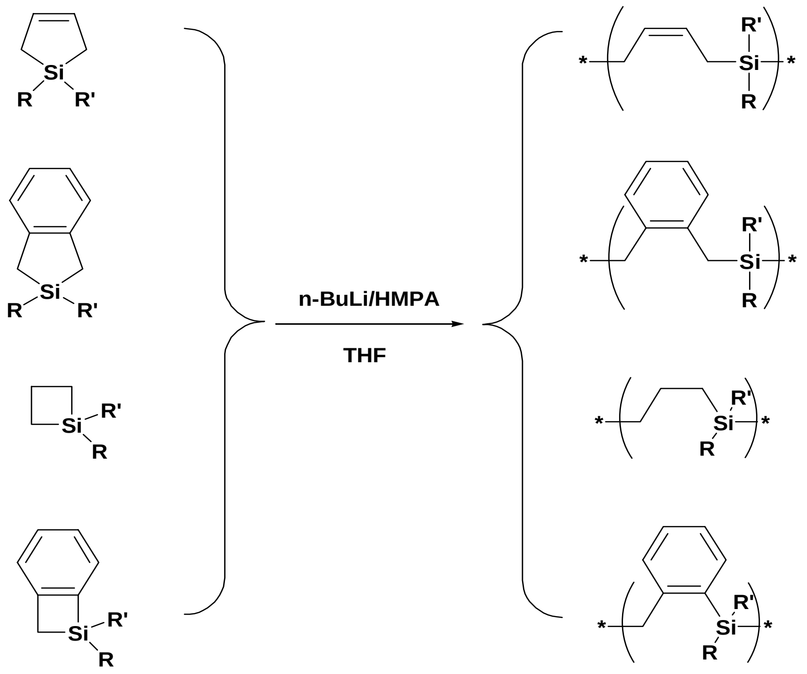
Birot et al[237,238] reported the synthesis of poly(methylsilmethylene)s or polysilapropylene starting from 1,1,3,3-tetramethyl-1,3-disilacyclobutane, it was previously described as an ionic reaction. The polymers were thermally stable upto 600°C under inert atmosphere. Substitution of methyl groups by chlorine atoms was achieved by trimethylchlorosilane with an $AlCl_3$ catalyst. Subsiquent reduction of chlorine containing polymers by $LiAlH_4$ gave hydrogenopolymers.



Scheme 7: Synthesis of PCS from 1,1,3,3-tetramethyl-1,3-disilacyclobutane

Yajima's PCS have high softening temperature because of branched structure. Seyferth[239] has proposed a modification of poly (dimethylsilmethylene) by deprotonation of the methylene groups at low temperature with strong bases such as n-BuLi or t-BuOK. Functionalization was achieved by addition of dimethylchlorosilane and/or vinyldimethyl chlorosilane.

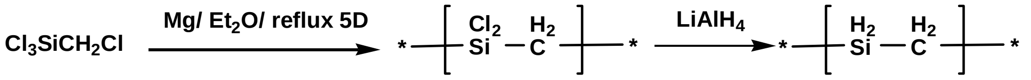
Weber et al,[239-243] have described the anionic ring-opening polymerization of various 1-silacyclopent-3-enes, 3,4-benzosilacyclopentenes, silacyclobutane or 2,3-benzosilacyclobutanes with n-BuLi/HMPA as catalyst. The polymers gave low char yield. They become higher when vinyl or SiH_2 groups were present, which might reflect the branched nature of the polymer as well as cross-linking *via* hydrosilylation reaction.



Scheme 8: Synthesis of PCSs by ring opening polymerization

1.7.2.2. Polycondensation of chloromethylchlorosilane

This section discusses about the synthesis of polycarbosilanes directly from chloromethylchlorosilanes.[244,246] Polycondensation of chloromethylchlorosilanes, chlorosilanes with methylene halides, chlorosilanes with acetylides, chlorosilanes with unsaturated hydrocarbons gives polycarbosilanes. As (chloromethyl)dimethyl chlorosilanes possess the desired Si-CH_2 units, it has been naturally used in the SiC precursor chemistry, but usually as a minor comonomer to avoid the introduction of large amounts of carbon and because the –$MeSiCH_2$- fragment is not a cross-linking site. Whitemarsh and Interrante[247] have prepared a highly branched PCS by Grignard coupling of (chloromethyl)trichlorosilane with Mg in diethyl ether, followd by reduction with $LiAlH_4$. The addition of CuCN catalyst was found to increase the molecular weight during the Grignard reaction,[248] and *in situ* reduction improved the overall yield. The head to tail coupling occurred during the polymerization.



Scheme 9: Synthesis of PCS by polycondensation of chloromethylchlorosilane

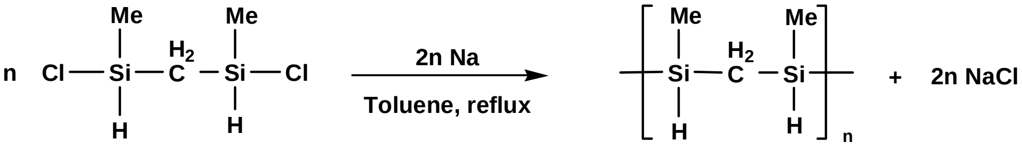
(Chloromethyl) trichlorosilane leads to an attractive precursor which is surprisingly claimed not to be very oxygen sensitive. It's cross-linking temperature and molecular weight might raise problems in fiber preparation; however, it could be suitable for matrix application. In 1993, DuPont disclosed[249] the synthesis of polycarbosilane from $Cl_2CHSiMeCl_2$, by using both Grignard and Wurtz coupling reactions. Compounds such as (dichloromethyl)methyldichlorosilane, $Cl_2CHSiMeCl_2$, and bis(chloromethyl)dichlorosilane, $(ClCH_2)_2SiCl_2$ have functional groups corresponding to an A_2B_2 type monomer. Both of these compounds are by-products of the synthesis of chloromethylmethyldichlorosilane. The polymers described in the patent were originally called "cross-linked polycarbosilane" instead of hyperbranched polymers. The patent authors found that Wurtz type coupling reaction of $Cl_2CHSiMeCl_2$ by metallic sodium formed an insoluble solid of formula $[MeSiCH]_n$. It is well known that, in addition to Si-C bonds, the Wurtz coupling reaction also generate both C-C and Si-Si units. Thus, the polymer made from $Cl_2CHSiMeCl_2$ by Wurtz reaction is likely to have a polycarbosilane/ polysilane network structure. The products of these reactions generally consist of a polydispersed mixture of oligomers and polymers that are coupled primarily through Si-C bonds, but which can also contain appreciable Si-Si bonding. Seyferth et al have also used dehalocoupling of $MeHSiCl_2$ with Na as a synthetic route to polymethylsilane.[250]

In the majority of cases, these are "one-pot" reactions that employ monomers that bear halogen or alkoxy groups on the C and Si end of the unit.

Indeed, hyperbranched polycarbosilanes have been described, in general, as "obtained in one synthetic step *via*, random, one-pot polymerization of multifunctional monomers of ABn type". The Wurtz coupling reaction, which employs alkali metals, can be used but as noted above, it generally leads to appreciable Si-Si and C-C bonding, in addition to Si-C bonding, and extensive cross-linking. In addition to the use of nucleophilic reactions to form a hyperbranched polycarbosilane backbone, this technique has also been used extensively to add side chains and otherwise modify the structure of the initially obtained polycarbosilane through reaction with Si-Cl or Si-OR groups on the polymer backbone. Thus, this methodology has been, and is likely to continue to be, an important component of the chemical tool kit that is available for the preparation and effective utilization of this important class of organosilicon polymers. This route proves to be a relatively easy way to prepare PCSs, but the structure and composition of the obtained precursors are difficult to control.

1.7.2.3. Copolymers with 1,3-dichloro-1,3-disilylmethanes

Polydimethylsilane is a highly microcrystalline solid, soluble only at high temperature in uncommon solvents. Several research groups have attempted to prepare copolysilanes. The lack of crystallinity increases the solubility. This approach helps to synthesize polysilacarbosilanes (PSCS) that could be easily transformed into SiC ceramic, on pyrolyzing. Polymerization by thermolysis of 1,3-dichloro-1,3-disilylmethanes and dichlorosilanes in the presence of alkali metal resulted in soluble greasy products.[251]



Scheme 10: Synthesis of PCS from 1,3-dichloro-1,3-disilylmethanes

Monomer, 1, 3-dichloro-1,3-disilylmethanes, can be prepared by silylation of methylene chloride.

$$CH_2Cl_2 + R_1R_2SiCl_2 + 2\,Mg \xrightarrow[Zn]{THF} (R_1R_2ClSi)_2CH_2$$

Scheme 11: Preparation of 1,3-dichloro-1,3-disilylmethanes

In this reaction Zinc is needed to allow the reaction to proceed; its role is not clearly understood. Zinc is suggested to mechanically clean and possibly activate the magnesium surface.[203]

Soluble PSCSs exhibit low TGA residue because they are not significantly cross-linked. A thermal treatment at 450-500°C under inert gas atmospheric pressure, afforded PCSs. This strategy has allowed to prepare organosilicon polymers which could be transformed into spinnable ceramic precursors at lower temperature and without using an autoclave. Adjustable C/Si ratios were obtained in the ceramic by varying the substituents; hydrogen decreases this ratio where as the presence of phenyl a group strongly increases it.

1.7.2.4. Polycondensation of chlorosilanes with methylene halides

Sartori *et al*[252] have prepared a series of PCSs by condensation of dichlorosilanes and methylene bromide with sodium in Xylene and studied their transformation into ceramics. They also investigated the halogenation of poly(diphenylsilmethylene) or poly(methylphenylsilmethylene) with hydrogen halides and catalytic amounts of aluminium halides.

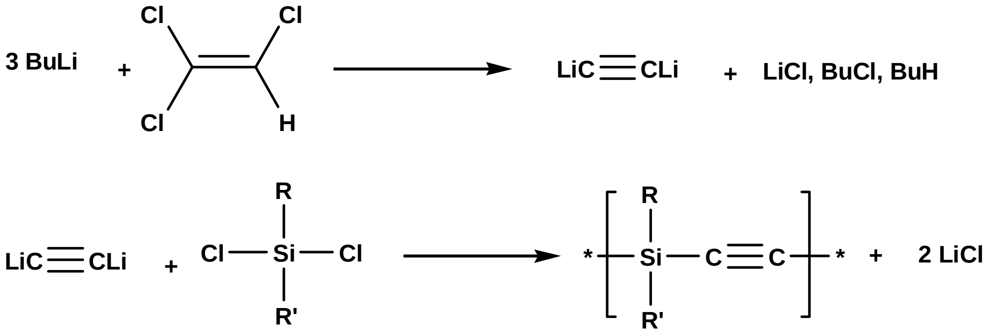
$$CH_2Br_2 + PhMeSiCl_2 + 4n\,Na \longrightarrow (PhMeSiCH_2)n + 2n\,NaCl + 2n\,NaBr$$

Scheme 12: Synthesis of PCS by polycondensation of chlorosilane with methylene bromide

Generally, PCS prepared from dihalomethanes are obtained in good yields but moderate molecular weight. In particular, the use of the inexpensive methylene chloride seems to be an alternative to the Yajima PCS if fibers can be easily obtained from polymers with Si-H bonds.

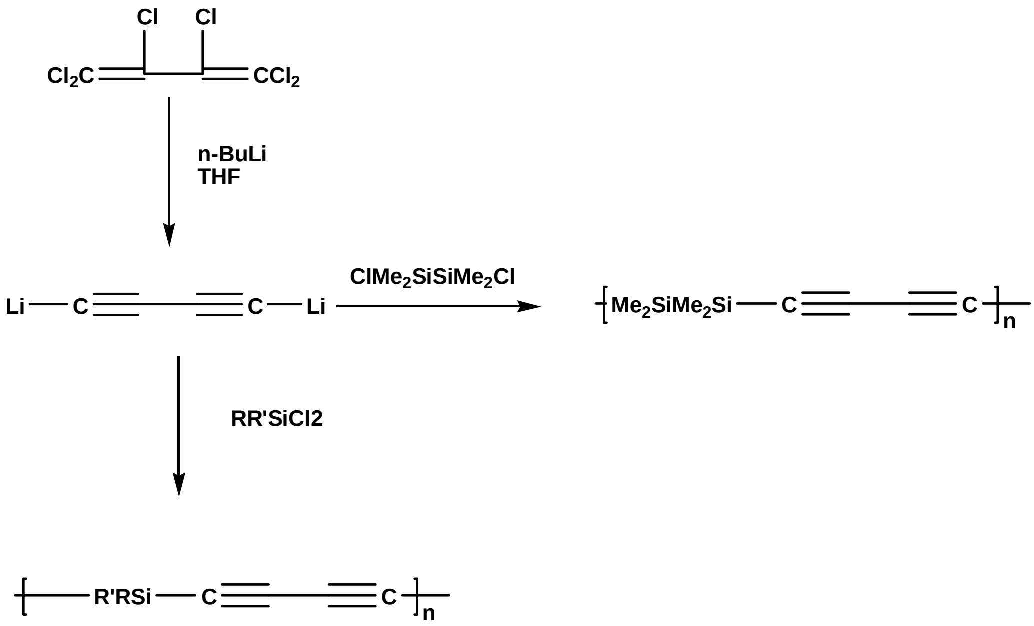
1.7.2.5. Polycondensation of chlorosilanes with acetylides

Barton's and Corriu's groups have almost simultaneously investigated the use of poly(silylacetylene)s as precursors to SiC fibres. These soluble polymers are easily prepared by co-condensation of dichlorosilanes with dilithioacetylenes.



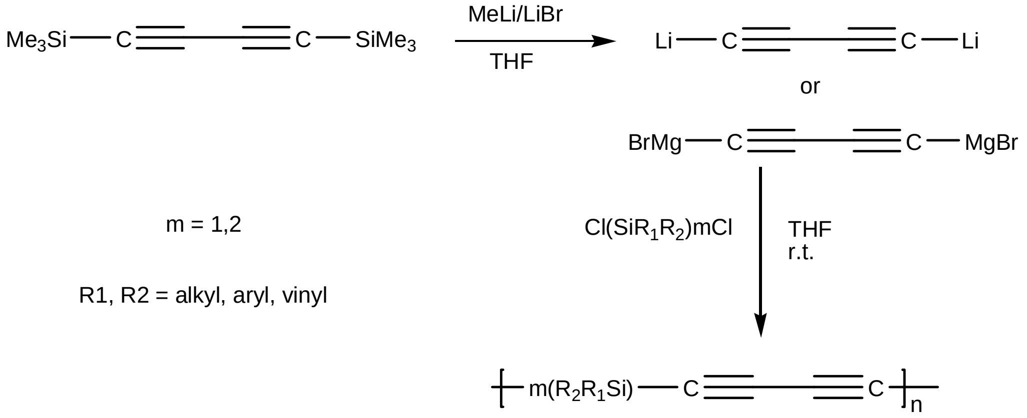
Scheme 13: PCS synthesis by polycondensation of chlorosilanes with dilithioacetylenes

Barton *et al*[253] have synthesized poly(silyldiacetylene)s or poly (disilyldiacetylene)s with hexachlorobutadiene as starting material, with average molecular weights.



Scheme14: PCS synthesis by polycondensation of hexachlorobutadiene with dilithioacetylenes

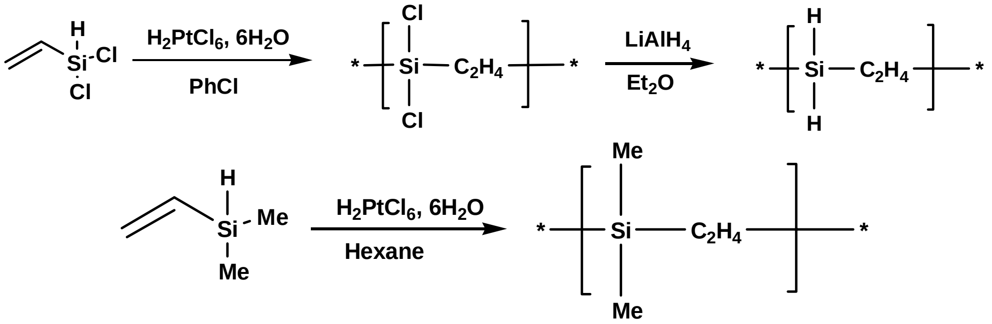
Corriu[254] prepared poly(silyldiacetylene)s from dichlorosilanes and diacetylene dilithium or di-Grignard reagents.



Scheme 15: Preparation of PCS by polycondensation of dichlorosilanes and diacetylene dilithium, di-Grignard reagents

1.7.2.6. Hydrosilylation reactions

Curry *et al*[255,,256] first described about the preparation of polycarbosilane by the hydrosilylation of vinylhydrogenosilanes, using Pt on carbon as catalysts. They have applied this method to prepare linear poly(silethylene)s, using Pt or Rh derivatives as catalysts.



Scheme 16: PCS preparation by the hydrosilylation

Thermal degradation was investigated for these polymers. Both fragmentation and cross-linking mechanisms appear to be strongly dependent on the substituents on the silicon atoms. Random homolytic chain cleavage accounts for the formation of the volatile and gaseous products detected during the degradation of the polymers, where as silylene intermediates have been suggested to explain the facile elimination of hydrogen at 380°C, as well as the formation of Si-H and Si-C bonds. More over, silylenes would explain the cross-linking *via* the formation of Si-Si bonds (which could come from dehydrocondensation), followed by the Kumada rearrangement.

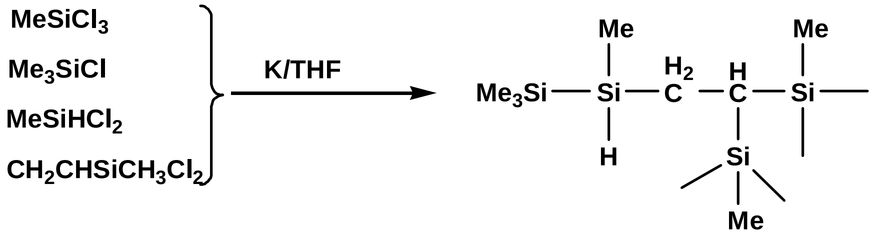
1.7.2.7. Polycondensation of chlorosilanes with unsaturated hydrocarbons

The preparation of PCSs by reacting chlorosilanes with unsaturated compounds in the presence of a metallic reducing agent has been shown, leading to polymer with high contents of carbon.[257]

$$CH_3SiHCl_2 + H_2C{=}CHSiCH_3Cl_2 \xrightarrow{K} (CH_3SiH)x(CH_2CHSiCH_3)y(CH_3Si)z$$

Scheme 17: PCS by polycondensation of chlorosilane with vinylsilane

Schilling[258] first synthesized mixed polymers by dechlorinating silanes with potassium. The presence of branched silyl units in the polymer backbone was critical to provide significant ceramic yields.



Scheme 18: Synthesis of mixed polymer by dechlorinating silanes

Preceding Schilling's work, Peterson and Arkles[259] reported a synthesis of cyclooligosilanes by the reaction of chlorohydrosilanes with lithium or lithium-alkali metal alloys. Brown-Wensley and Sinclair,[260,261] and Bryson and Noireaux *et al*[262] have prepared partly cross-linked PMS by the reaction of CH_3SiHCl_2 with Na in THF.

TG-DTA study of polycarbosilanes up to 1200 ^{0}C was considered[263]. At the first stage (from room temperature to 360^0 C), the small weight loss was observed as a result of evaporation of low-molecular-weight fractions. No obvious change occurred in this stage. As the temperature was increased further (from 360^0 to 585^0 C), the TG curve fell off rapidly as the result of evaporation of low-molecular-weight fractions and evolution of H_2 and CH_4 due to dehydrogenation and dehydrocarbonation condensation among the PCS molecules. A weight loss of 11% took place. At this stage, the network structure was gradually formed by thermal curing. At the third stage (from 585^0 to 800^0 C), the DTA curve exhibited a large endothermic peak. The weight loss about

7% took place. The reaction at this stage consisted mainly of thermal decomposition of the side chains such as Si-H, Si-CH_3, and C-H in Si-CH_2-Si of the PCS. Soluble PCS exhibited low TGA residue because they were not significantly cross-linked.

It is clear that the various substituents (hydrogen and other pendant groups) play a crucial role on the polymer properties, its thermal behaviour, and the pyrolysis mechanisms.

1.7.3. Metal containing polycarbosilanes

The preparation of polymers having reactive (Cl, OR or H) functionalities attached to the silicon and then introduction of the desired substituents have been achieved through substitution or addition reactions. A variety of different end-groups can be substituted for further modifications. The Si-H bonds are more reactive than the C-H bonds. So when we are treating metal reagents with the polymer, Si-M bonds are formed preferentially. Metal-containing polymers are attracting growing attention as functional materials,[264] the presence of transition metal centres in a polymer has enabled redox control of the size and shape of a macroscopic object; selective binding and sensing of small molecules, metal ions, and biomolecules and the introduction of desirable catalytic property[265].

Most of the metallopolymers reported have the draw back that they possess low metal concentration. There is probability for the bond formation of Si-M bonds in each Si atoms of the pendant group. As the reactivity of the Si-X bond is high (X= Cl, OR or H),[266] by using polycarbosilanes that draw back can be avoided.

PCS can be used as a binder for transition metals. Such a synthesis is based on the well-known reactivity of the Si-H bond towards metal carbonyl/

metallocenes/ metal oxides. The introduction of metal atoms into polymers is of interest as a means of creating functional macromolecular and supramolecular materials, which combine processability with interesting redox, optical, electronic, preceramic and catalytic properties.

It is important to note that all monomers are not incorporated at the same rate, in a free radical copolymerization of two monomers, A and B, the rate at which a given monomer is copolymerized depends on the reactivity of the monomer, the reactivity of the free radical derived from the monomer and how these two reactivities compare with the corresponding reactivities of the other monomer and its derived radical.[267]

The introduction of functionality onto the polymer support can often be readily achieved simply by treating a polymer as a structural analogue of a low molecular weight species and then utilizing identical chemistry to achieve a desired derivatisation or structural elaboration.[267] An alternative or complementary approach to introduce a specific functionality during polymerization is by utilizing a comonomer which already carries the required function or some precursor group which can be subsequently be readily transformed. This approach can be useful in producing a structurally well-defined polymer, for controlling the proportion of functional groups introduced and for providing some information on the distribution of the groups along the polymer chain.

^{29}Si NMR is possibly the most significant method for the silicon analysis[268]. The major problem associated with ^{29}Si NMR spectroscopy is its poor sensitivity, because of low isotopic abundance, long relaxation times and an unfavourable overhauser effect – appear to have been solved by the use of shiftless relaxation reagents in combination with heteronuclear decoupling and Fourier Transform spectroscopy.

1.8. Dendrimers

Dendrimers[269] are repeatedly branched, roughly spherical macromolecules. A dendrimer is typically symmetric around the core, and often adopts a spherical three-dimensional morphology. Dendrimers can be considered to have three main parts: a central part called core, an inner shell, and an outer shell. Ideally, a dendrimer can be synthesized to have different functionality in every part to control properties such as solubility, thermal stability, and attachment of compounds for various applications. Synthetic processes can also precisely control the size and number of branches on the dendrimer. There are two distinct routes of dendrimer synthesis, divergent synthesis and convergent synthesis. However, because the actual reactions consist of many steps, it is difficult to synthesize dendrimers using either method. This makes dendrimers hard to make and very expensive to obtain.

1.8.1. Divergent method

The dendrimer is gathered from a multifunctional core, which is extended outward by a series of reactions. Each step of the reaction must be driven to full completion to prevent mistakes in the dendrimer, which can cause trailing generations. Such impurities can impact the functionality and symmetry of the dendrimer, but are extremely difficult to purify out because the relative size difference between perfect and imperfect dendrimers is very small.

1.8.2. Convergent method

Dendrimers are built from small molecules that end up at the surface of the sphere, and reactions proceed building inward and are eventually attached to a core. This method makes it much easier to remove impurities and shorter branches along the way, so that the final dendrimer is more monodisperse. However dendrimers made in this way are not as large as those made by divergent methods because crowding due to steric effects along the core is limiting

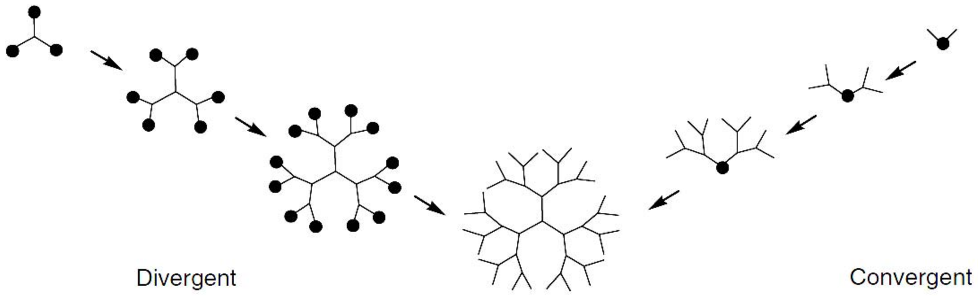


Figure 13: Methods used for the dendrimer preparation

1.8.3. Applications of dendrimers

Applications of dendrimers typically involve conjugating other chemical species to the dendrimer surface that can function as detecting agents, as a dye molecule, affinity ligands, targeting components, radioligands, imaging agents, or pharmaceutically active compounds. Dendrimers have very strong potential for these applications because their structure can lead to multivalent systems. In other words, one dendrimer molecule has hundreds of possible sites to couple to an active species. Researchers have aimed to utilize the hydrophobic environments of the dendritic media to conduct photochemical reactions that generate the products that are synthetically challenged. Carboxylic acid and phenol terminated water soluble dendrimers were synthesized to establish their utility in drug delivery as well as conducting chemical reactions in their interiors.[270]

The field of dendrimers[271] was developed in the late 1970s and early 1980s[272-277] and has attained great interest during the past decade.[278-292] This condition is because, beyond the aesthetics appeal, to their great potential of applications in biology and materials science. Among the main potential applications of dendrimers, catalysis stands as one of the most promising applications. Indeed, dendrimers offer a unique opportunity to combine the advantages of homogeneous and heterogeneous catalysis yet keeping the well-defined molecular features required for a fully detailed analysis of the catalytic events.[293] It is possible to tune the structure, size, shape, and solubility of dendrimers and metallodendrimers at will and to locate catalytic sites at the core or at the periphery.[290] It is possible to remove the catalyst from the reaction medium after a reaction carried out in the presence of a metallodendritic catalyst. This is achieved by precipitation or by techniques as ultrafiltration or ultracentrifugation. Membrane reactors are presently developed for this purpose. Organometallic and inorganic catalysts[294-298] supported on organic polymers such as polystyrene or inorganic polymers such as silica have been investigated,[299-302]. The field of dendrimers has been frequently reviewed,[271,278-292] and catalytic applications have been commonly mentioned.[288,289] It is becoming more and more obvious that dendritic catalysts will be applicable in the close future. New segments of nanostructured materials with well-defined porosities have potential applications in catalysis,[299-302] and some of them are made from dendrimers. The broadest class of dendritic catalysts is related to homogeneous catalysis, although some supported and heterogeneous dendritic catalysts also have appeared now-a-days. Moreover, the field of dendritic catalysts and dendrimers in catalysis spreads into various areas of organic, inorganic, materials, biological, and polymer chemistry.

Since their introduction in the mid-1980s, the novel class of dendrimer architecture has been a prime candidate for hosts-guest chemistry.[271] Dendrimers with hydrophobic core and hydrophilic periphery have shown to exhibit micelle-like behavior and have container properties in solution.[278] The use of dendrimers as unimolecular micelles was proposed by Newkome in

1985.[303] This analogy highlighted the utility of dendrimers as solubilizing agents,[276] the majority of drugs available in pharmaceutical industry are hydrophobic in nature and this property in particular creates major formulation problems. This drawback of drugs can be improved by dendrimeric scaffolding, which can be used to encapsulate as well as to solubilize the drugs because of the capability of such scaffolds to participate in extensive hydrogen bonding with water.[304-308] The scientists were persistently trying to manipulate dendrimer's solubilizing trait, in their way to explore dendrimer as drug delivery [309,310] and target specific carrier.[311-313]

The expression "organic catalyst" has recently been introduced to define an organic compound capable of promoting a given transformation in substoichiometric quantity.[314] In this context, organic means metal-free, and it is used to differentiate this class of catalysts from that of metal-based catalytic species. Implicitly, however, the term organic emphasizes the advantages of performing a catalytic reaction under metal-free conditions. These advantages might include, as , the possibility of (i) working in wet solvents and under an aerobic atmosphere, (ii) dealing with a stable and robust catalyst, and (iii) avoiding from the outset the problem of the leaching of a toxic metal into the organic product. Organic catalysts can be seen as minimalistic versions of enzymes, from which they are conceptually derived and to which are often compared.[315] Even if only in some cases they display the remarkable selectivity peculiar of enzymes, organic catalysts generally are more stable, less expensive, and enjoy a wider application under a variety of conditions unsustainable by enzymes. In addition, organic catalysts are also more readily amenable than both metal-based and biocatalysts to anchoring on a support with the aim of facilitating catalyst recovery and recycling. As far as enzyme supporting is concerned, in principle, one can expect the connection to a support to have a deeper impact on the complex structure of an enzyme (and, hence, on its properties) than on that of a simple organic derivative. Moreover, the introduction of several units of a catalyst on a polymer support with many reactive sites seems more feasible in the case of a small molecule than in that of a large biocatalyst. On the other hand, it has repeatedly been shown that immobilization of a metal-based catalyst on a support is often affected by extensive metal leaching and often requires catalyst regeneration by metal replenishment before recycling. The development of a polymer-supported version of an organic catalyst has quite timely followed that of the catalyst itself since the benefits of catalyst recovery and recycling became compellingly evident to the very first researchers in the field. This tendency has exploded in recent years, which have witnessed a tremendous growth of chemists' interest in synthetic methods based on supported reagents and catalysts[319] has recently been devoted to recoverable catalysts and reagents.[320-322] The use of organic catalysts bound to inorganic supports will be considered only when these catalysts are particularly important, when they are the only existing examples of a supported organic catalyst, or when the comparison between systems immobilized onto inorganic and organic supports appears particularly relevant.[316-322]

Multicomponent Reactions (MCRs) are convergent reactions, in which three or more starting materials react to form a product, where basically all or most of the atoms contribute to the newly formed product. In an MCR, a product is assembled according to a cascade of elementary chemical reactions. Thus, there is a network of reaction equilibria, which all finally flow into an irreversible step yielding the product. The challenge is to conduct an MCR in such a way that the network of pre-equilibrated reactions channel into the main product and do not yield side products. The result is clearly dependent on the reaction conditions: solvent, temperature, catalyst, concentration, the kind of starting materials and functional groups. Such considerations are of particular importance in connection with the design and discovery of novel MCRs.[323]

The present thesis is concerned with the preparation and evaluation of catalytic activity of certain metal containing polycarbosilanes. The results of the investigations carried out in this direction are presented in the following chapters. One chapter has been dedicated for the results of the investigation on catalysis by polysilane dendrimer bearing terminal amino groups.

1.9. Materials and methods

FTIR spectra were recorded on JASCO model 4100 FTIR spectrometer as KBr pellets. Solid state ^{29}Si-CP-MAS NMR spectra were obtained from NMR research centre, IISc. Bangalore. TG-DTA analysis was done on Perkin-Elmer Diamond model TG/DTA system using Platinum as standard. Samples were heated under nitrogen atmosphere from 50^{o}C- 1000^{o}C at a rate of 20^{o}C/min. The X- Ray Diffraction analysis was carried out using Rigaku X-ray Photometer at SAIF, CUSAT. The sample was scanned over the range of 20^{o}-90^{o} angles with an increment of 0.05 ^{o} angle and with the rotation speed of 5^{o}/min., Surface Area & porosity were measured using- TriStar 3000 V6.07 A of Micromeritics at Süd-chemie-Cochin, EPR spectra were recorded from Bharathidasan University, Trichy, ^{1}H NMR spectra were recorded on Bruker 400 MHz instrument with TMS as the internal standard in $CDCl_3$ (NMR research centre, IISc, Bangalore and SAIF, STIC, CUSAT, Kochi, Kerala). In catalytic activity study each of the products was analyzed for purity by HPLC on Shimadzu CLASS VP Ver 6.1. Column: Phenomenex Luna 5u C18 (2) 100 Å. The Flow rate, detector wavelength and the temperature were 1mL/minute, 254nm and 28^{0}C respectively.

1.10. References

1. Merrifield, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2149.
2. Molnar, A. *Chem. Rev.* **2011,** *111*, 2251.
3. Baker, R. T.; Kobayashi, S.; Leitner, W. *Adv. Synth. Catal.* **2006**, *348*, 1337.
4. Horvath, I. T.; Anastas, P. T. *Chem. Rev.* **2007**, *107*, 2169.
5. Climent, M. J.; Corma, A.; Iborra, S. *Chem. Rev.* **2011**, *111,* 1072.
6. Vagin, S. I.; Reichardt, R.; Klaus, S.; Rieger, B. *J. Am. Chem. Soc.* **2010**, *132*, 14367.
7. Challa, G. *J. Mol. Catal.* **1983**, *2*, 1.
8. Signori, A. M.; Santos, K. O.; Eising, R.; Albuquerque, B. L.; Giacomelli, F. C.; Domingos, J. B. *Langmuir* **2010**, *26(22)*, 17772.
9. Yamada, Y. M. A.; Jin, C. K.; Uozumi, Y. *Org. Lett.,* **2010,** *12*, 4540.
10. Ley, S. V.; Baxendale, I. R.; Bream, R. N.; Jackson, P. S.; Leach, A. G.; Longbottom, D. A.; Nesi, M.; Scott, J. S.; Storer, R. I.; Taylor, S. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3815.
11. Karimi, B.; Akhavan, P. F. *Inorg. Chem*. **2011**, *50*, 6063.
12. Bergbreiter, D. E.; Yang, Y. C.; Hobbs, C. E. *J. Org. Chem.* **2011**, *76*, 6912.
13. McNamara, C. A.; Dixon, M. J.; Bradley, M. *Chem. Rev.* **2002**, *102*, 3275.
14. Benaglia, M.; Puglisi, A.; Cozzi, F. *Chem. Rev.* **2003**, *103*, 3401.
15. Kirschning, A.; Monenschein, H.; Wittenberg, R. *Angew. Chem., Int.Ed.* **2001**, *40*, 650.

16. Yoshida, J.; Itami, K. *Chem. Rev.* **2002**, *102*, 3693.

17. Pomogailo, A. D. *Catalysis by Polymer-Immobilized Metal Complexes*; **1998**, Australia, Gordon and Breach.

18. Kobayashi, S. *Chem. Soc. Rev.* **1999**, *28*, 1.

19. Ikegami, S.; Hamamoto, H. *Chem. Rev.* **2009,** *109,* 583

20. Senkan, S. *Angew. Chem., Int. Ed.* **2001***, 40*, 312.

21. Reetz, M. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 284

22. Hodge, P. *Chem. Soc. Rev.* **1997**, *26*, 417.

23. Vaino, A. R.; Janda, K. D. *J. Comb. Chem.* **2000**, *2*, 579.

24. Santini, R.; Griffith, M. C.; Qi, M. *Tetrahedron Lett.* **1998**, *39*, 8951.

25. Vaino, A. R.; Goodin, D. B.; Janda, K. D. *J. Comb. Chem.***2000**, *2*, 330.

26. Walsh, D. P.; Pang, C.; Parikh, P. B.; Kim, Y. S.; Chang, Y. T. *J. Comb. Chem.* **2002**, *4*, 204.

27. Mutter, M.; Hagenmaier, H.; Bayer, E. *Angew. Chem., Int. Ed.***1971**, *10*, 811.

28. Bayer, E. *Angew. Chem., Int. Ed.* **1991**, *30*, 113.

29. Hudson, D. *J. Comb.Chem.* **1999**, *1*, 403

30. Lu, J.; Toy, P. H. *Chem. Rev.* **2009,** *109,* 815.

31. Bergbreiter, D. E. *Chem. Rev.* **2002**, *102*, 3345.

32. Bergbreiter, D. E.; Sung, S. D. *Adv. Synth. Catal.* **2006**, *348*, 1352.

33. Gravert, K. D.; Janda, K. D. *Chem. Rev.* **1997**, *97*, 489.

34. Dickerson, T. J.; Reed, N. N.; Janda, K. D. *Chem. Rev.* **2002**, *102*, 3325.

35. Lee, T. K.; Ryoo, S. J.; Byun, J. W.; Lee, S. M.; Lee, Y. S. *J. Comb.Chem.* **2005**, *7*, 170.

36. Lee, T. K.; Lee, S. M.; Ryoo, S. J.; Byun, J. W.; Lee, Y. S. *Tetrahedron Lett.* **2005**, *46*, 7135.

37. Kim, J. H.; Jun, B. H.; Byun, J. W.; Lee, Y. S. *Tetrahedron Lett.* **2004**, *45*, 5827

38. Kim, J. H.; Kim, J. W.; Shokouhimehr, M.; Lee, Y. S. *J. Org. Chem.* **2005**, *70*, 6714.

39. Shokouhimehr, M.; Kim, J.H.; Lee, Y. S. *Synlett* **2006**, 618.

40. Kim, J. H.; Lee, D. H.; Jun, B. H.; Lee, Y. S. *Tetrahedron Lett.* **2007**, *48*, 7079.

41. Helms, B.; Guillaudeu, S. J.; Xie, Y.; McMurdo, M.; Hawker, C. J.; Fre´chet, J. M. J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6384.

42. Chi, Y.; Scroggins, S. T.; Fre´chet, J. M. J. *J. Am. Chem. Soc.* **2008**, *130*, 6322

43. Wang, Y.; Zhang, G.; Yan, H.; Fan, Y.; Shi, Z.; Lu, Y.; Sun, Q.; Jiang, W.; Zheng, Y.; Li, S.; Liu, Z. *Tetrahedron Lett.* **2006**, *62*, 4948.

44. Toy, P. H.; Janda, K. D. *Tetrahedron Lett.* **1999**, *40*, 6329.

45. Toy, P. H.; Reger, T. S.; Garibay, P.; Garno, J. C.; Malikayil, J. A.; Liu, G.Y.; Janda, K. D. *J. Comb. Chem.* **2001**, *3*, 117.

46. Choi, M. K. W.; Toy, P. H. *Tetrahedron* **2004**, *60*, 2903

47. Lau, K. C. Y.; He, H. S.; Chiu, P.; Toy, P. H. *J. Comb. Chem.***2004**, *6*, 955.

48. He, H. S.; Zhang, C.; Ng, C. K.W.; Toy, P. H. *Tetrahedron* **2005**, *61*, 12053.

49. Zhao, L. J.; He, H. S.; Shi, M.; Toy, P. H. *J. Comb. Chem.***2004**, *6*, 680.

50. Choi, M. K. W.; Toy, P. H. *Tetrahedron* **2004**, *60*, 2875.

51. Chung, C. W. Y.; Toy, P. H. *Tetrahedron* **2005**, *61*, 709.

52. Moss, J. A.; Dickerson, T. J.; Janda, K. D. *Tetrahedron Lett.* **2002**, *43*, 37.

53. Lee, S. H.; Clapham, B.; Koch, G.; Zimmermann, J.; Janda, K. D. *Org. Lett.* **2003**, *5*, 511.

54. Matsushita, H.; Lee, S. H.; Joung, M.; Clapham, B.; Janda, K. D. *Tetrahedron Lett.* **2004**, *45*, 313

55. Toy, P. H.; Reger, T. S.; Janda, K. D. *Org. Lett.* **2000**, *2*, 2205.

56. Harned, A. M.; He, H. S.; Toy, P. H.; Flynn, D. L.; Hanson, P. R. *J. Am. Chem. Soc.* **2005**, *127*, 52.

57. Akiyama, R.; Kobayashi, S. *J. Am. Chem. Soc.* **2003**, *125*, 3412

58. Okamoto, K.; Akiyama, R.; Kobayashi, S. *J. Org. Chem.* **2004**, *69*, 2871.

59. Okamoto, K.; Akiyama, R.; Kobayashi, S. *Org. Lett.* **2004**, *6*, 1987.

60. Hagio, H.; Sugiura, M.; Kobayashi, S. *Org. Lett.* **2006**, *8*, 375.

61. Okamoto, K.; Akiyama, R.; Yoshida, H.; Yoshida, T.; Kobayash, S. *J. Am. Chem. Soc.* **2005**, *127*, 2125.

62. Akiyama, R.; Sagae, T.; Sugiura, M.; Kobayashi, S. *J. Organomet. Chem.* **2004**, *689*, 3806.

63. Nishio, R.; Wessely, S.; Sugiura, M.; Kobayashi, S. *J. Comb. Chem.* **2006**, *8*, 459.

64. Takeuchi, M.; Akiyama, R.; Kobayashi, S. *J. Am. Chem. Soc.* **2005**, *127*, 13096.

65. Miyamura, H.; Akiyama, R.; Ishida, T.; Matsubara, R.; Takeuchi, M.; Kobayashi, S. *Tetrahedron* **2005**, *61*, 12177.

66. Hagio, H.; Sugiura, M.; Kobayashi, S. *Synlett* **2005**, 813.

67. Miyamura, H.; Shiramizu, M.; Matsubara, R.; Kobayashi, S. *Chem. Lett.* **2008**, *3*, 360.

68. Lee, C. K. Y.; Holmes, A. B.; Ley, S. V.; McConvey, I. F.; Al-Duri, B.; Leeke, G. A.; Santos, R. C. D.; Seville, J. P. K. *Chem. Commun.* **2005**, 2175.

69. Sharma, A. K.; Gowdahalli, K.; Krzeminski, J.; Amin, S. *J. Org. Chem.* **2007**, *72*, 8987.

70. Quai, M.; Repetto, C.; Barbaglia, W.; Cereda, E. *Tetrahedron Lett.* **2007**, *48*, 1241.

71. Shirley, I. M. *Org. Lett.* **2003**, *5*, 185.

72. Bolfa, C.; Zoleo, A.; Sassi, A. S.; Maniero, A. L.; Pears, D.; Jerabek, K.; Corain, B. *J. Mol. Catal. A: Chem.* **2007**, *275*, 233.

73. Richardson, J. M.; Jones, C. W. *Adv. Synth. Catal.* **2006**, *348*, 1207.

74. Hultzsch, K. C.; Jernelius, J. A.; Hoveyda, A. H.; Schrock, R. R. *Angew. Chem., Int. Ed.* **2002**, *41*, 589.

75. Seebach, D.; Beck, A. K.; Heckel, A. *Angew. Chem., Int. Ed.* **2001**, *40,* 92.

76. Alesso, S. M.; Yu, Z.; Pears, D.; Worthington, P. A.; Luke, R. W. A.; Bradley, M. *Tetrahedron* **2003**, *59*, 7163.
77. Zhao, L. J.; Kwong, C. K. W.; Shi, M.; Toy, P. H. *Tetrahedron* **2005**, *61*, 12026
78. Bergbreiter, D. E.; Sung, S. D.; Li, J.; Ortiz, D.; Hamilton, P. N. *Org. Process Res. Dev.* **2004**, *8*, 461.
79. Datta, A.; Plenio, H. *Chem. Commun.* **2003**, 1504.
80. Hillerich, J.; Plenio, H. *Chem. Commun.* **2003**, 3024.
81. Zhao, C.; Shi, S.; Mir, D.; Hurst, D.; Li, R.; Xiao, X. Y.; Lillig, J.; Czarnik, A. W. *J. Comb. Chem.* **1999**, *1*, 91.
82. Hodges, J. C.; Harikrishnan, L. S.; Ault-Justus, S. *J. Comb. Chem.* **2000**, *2*, 80.
83. Wisnoski, D. D.; Leister, W. H.; Strauss, K. A.; Zhao, Z.; Lindsley, C. W. *Tetrahedron Lett.* **2003**, *44*, 4321.
84. Pawluczyk, J. M.; McClain, R. T.; Denicola, C.; Mulhearn, J., Jr.; Rudd, D. J.; Lindsley, C. W. *Tetrahedron Lett.* **2007**, *48*, 1497.
85. Fournier, D.; Pascual, S.; Montembault, V.; Haddleton, D. M.; Fontaine, L. *J. Comb. Chem.* **2006**, *8*, 522.
86. Fournier, D.; Pascual, S.; Montembault, V.; Fontaine, L. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5316.
87. Bergbreiter, D. E.; Li, J. *Chem. Commun.* **2004**, 42.
88. Li, J.; Sung, S.; Tian, J.; Bergbreiter, D. E. *Tetrahedron* **2005**, *61*, 12081.
89. Bergbreiter, D. E.; Tian, J. *Tetrahedron Lett.* **2007**, *48*, 4499.

90. Bergbreiter, D. E.; Hamilton, P. N.; Koshti, N. M. *J. Am. Chem. Soc.* **2007**, *129*, 10666.

91. Hongfa, C.; Tian, J.; Bazzi, H. S.; Bergbreiter, D. E. *Org. Lett.* **2007**, *9*, 3259.

92. Hongfa, C.; Tian, J.; Andreatta, J.; Darensbourg, D. J.; Bergbreiter, D. E. *Chem. Commun.* **2008**, 975.

93. Barrett, A. G. M.; Hopkins, B. T.; Kobberling, J. *Chem. Rev.* **2002**, *102*, 3301.

94. Harned, A. M.; Zhang, M.; Vedantham, P.; Mukherjee, S.; Herpel, R. H.; Flynn, D. L.; Hanson, P. R. *Aldrichim.Acta* **2005**, *38*, 3.

95. Barrett, A. G. M.; Cramp, S. M.; Roberts, R. S.; Zecri, F. J. *Org. Lett.* **1999**, *1*, 579.

96. Barrett, A. G. M.; Cramp, S. M.; Roberts, R. S. *Org. Lett.* **1999**, *1*, 1083.

97. Lee, B. S.; Mahajan, S.; Clapham, B.; Janda, K. D. *J. Org. Chem.* **2004**, *69*, 3319.

98. Årstad, E.; Barrett, A. G. M.; Tedeschi, L. *Tetrahedron Lett.* **2003**, *44*, 2703.

99. Barrett, A. G. M.; Hopkins, B. T.; Love, A. C.; Tedeschi, L. *Org. Lett.* **2004**, *6*, 835.

100. Mayr, M.; Mayr, B.; Buchmeiser, M. R. *Angew. Chem., Int. Ed.* **2001**, *40*, 3839.

101. Krause, J. O.; Lubbad, S. H.; Nuyken, O.; Buchmeiser, M. R. *Macromol. Rapid Commun.* **2003**, *24*, 875.

102. Yang, L.; Mayr, M.; Wurst, K.; Buchemiser, M. R. *Chem.Eur. J.* **2004**, *10*, 5761.

103. Kroll, R. M.; Schuler, N.; Lubbad, S.; Buchmeiser, M. R. *Chem. Commun.* **2003**, 2742.

104. Mayr, M.; Wang, D.; Kroell, R.; Schuler, N.; Pruehs, S.; Fuerstner, A.; Buchmeiser, M. R. *Adv. Synth. Catal.* **2005**, *347*, 484.

105. Buchmeiser, M. R.; Lubbad, S.; Mayr, M.; Wurst, K. *Inorg. Chim. Acta* **2003**, *345*, 145.

106. Krause, J. O.; Lubbad, S.; Nuyken, O.; Buchmeiser, M. R. *Adv. Synth. Catal.* **2003**, *345*, 996.

107. Barrett, A. G. M.; Love, A. C.; Tedeschi, L. *Org. Lett.* **2004**, *6*, 3377.

108. Barrett, A. G. M.; Bibal, B.; Hopkins, B. T.; Ko¨bberling, J.; Love, A. C.; Tedeschi, L. *Tetrahedron* **2005**, *61*, 12033.

109. Fuchter, M. J.; Hoffman, B. M.; Barrett, A. G. M. *J. Org. Chem.* **2006**, *71*, 724.

110. Herpel, R. H.; Vedantham, P.; Flynn, D. L.; Hanson, P. R. *Tetrahedron Lett.* **2006**, *47*, 6429.

111. Stoianova, D. S.; Yao, L.; Rolfe, A.; Samarakoon, T.; Hanson, P. R. *Tetrahedron Lett.* **2008**, *49*, 4553.

112. Harned, A. M.; Sherrill, W. M.; Flynn, D. L.; Hanson, P. R. *Tetrahedron* **2005**, *61*, 12093.

113. Zhang, M.; Flynn, D. L.; Hanson, P. R. *J. Org. Chem.* **2007**, *72*, 3194.

114. Vedantham, P.; Zhang, M.; Gor, P. J.; Huang, M.; Georg, G. I.; Lushington, G. H.; Mitscher, L. A.; Ye, Q.-Z.; Hanson, P. R. *J. Comb. Chem.* **2008**, *10*, 195.

115. Yang, Y. C.; Luh, T. Y. *J. Org. Chem.* **2003**, *68*, 9870.

116. Tanyeli, C.; Gu¨mu¨s¸, A. *Tetrahedron Lett.* **2003**, *44*, 1639.

117. Yu, K. Q.; Sommer, W.; Richardson, J. M.; Weck, M.; Jones, C. W. *Adv. Synth. Catal.* **2005**, *347*, 161.

118. Sommer, W. J.; Yu, K.; Sears, J. S.; Ji, Y.; Zheng, X.; Davis, R. J.; Sherrill, C. D.; Jones, C. W.; Weck, M. *Organometallics* **2005**, *24*, 4351.

119. Holbach, M.; Weck, M. *J. Org. Chem.* **2006**, *71*, 1825.

120. Jain, S.; Zheng, X.; Jones, C. W.; Weck, M.; Davis, R. J. *Inorg. Chem.* **2007**, *46*, 8887.

121. Madhavan, N.; Weck, M. *Adv. Synth. Catal.* **2008**, *350*, 419.

122. Polo, E.; Forlini, F.; Bertolasi, V.; Boccia, A. C.; Sacchi, M. C. *Adv. Synth. Catal.* **2008**, *350*, 1544.

123. Nomura, K.; Ogura, H.; Imanishi, Y. *J. Mol. Catal., A: Chem.* **2002**, *185*, 311.

124. Nomura, K.; Kuromatsu, Y. *J. Mol. Catal., A: Chem.* **2006**, *245*, 152.

125. Chinchilla, R.; Dodsworth, D. J.; Na´jera, C.; Soriano, J. M. *Tetrahedron Lett.* **2001**, *42*, 4487.

126. Chinchilla, R.; Dodsworth, D. J.; Na´jera, C.; Soriano, J. M. *Tetrahedron Lett.* **2001**, *42*, 7579.

127. Chinchilla, R.; Dodsworth, D. J.; Na´jera, C.; Soriano, J. M. *Bioorg. Med. Chem. Lett.* **2002**, *12*, 1817.

128. Chinchilla, R.; Dodsworth, D. J.; Na´jera, C.; Soriano, J. M. *Synlett* **2003**, 809.

129. Chinchilla, R.; Dodsworth, D. J.; Na´jera, C.; Soriano, J. M. *Tetrahedron Lett.* **2002**, *44*, 463.

130. Chinchilla, R.; Dodsworth, D. J.; Na´jera, C.; Soriano, J. M.; Yus, M. *ARKIVOC* **2003**, 41.

131. Gil-Molto´, J.; Karlstro¨m, S.; Na´jera, C. *Tetrahedron* **2005**, *61*, 12168.

132. Bergbreiter, D. E.; Kippenberger, A.; Zhong, Z. *Can. J. Chem.* **2006**, *84*, 1343.

133. Bergbreiter, D. E.; Franchina, J. G.; Case, B. L. *Org. Lett.* **2000**, *2*, 393.

134. Kani, I.; Omary, M. A.; Rawashdeh-Omary, M. A.; Lopez-Castillo, Z. K.; Flores, R.; Akgerman, A.; Fackler, J. P., Jr. *Tetrahedron* **2002**, *58*, 3923.

135. Yao, Q.; Zhang, Y. *J. Am. Chem. Soc.* **2004**, *126*, 74.

136. Bastin, S.; Eaves, R. J.; Edwards, C. W.; Ichihara, O.; Whittaker, M.; Wills, M. *J. Org. Chem.* **2004**, *69*, 5405.

137. Beier, M. J.; Knolle, W.; Prager-Duschke, A.; Buchmeiser, M. R. *Macromol. Rapid Commun.* **2008**, *29*, 904.

138. Bergbreiter, D. E.; Case, B. L.; Liu, Y. S.; Caraway, J. W. *Macromolecules* **1998**, *31*, 6053.

139. Yamada, Y. M. A.; Tabata, H.; Ichinohe, M.; Takahashi, H.; Ikegami, S. *Tetrahedron* **2004**, *60*, 4087.

140. Delgado, M.; Spanka, C.; Kerwin, L. D.; Wentworth, P., Jr.; Janda, K. D. *Biomacromolecules* **2002**, *3*, 262.

141. Rogers, C. J.; Dickerson, T. J.; Wentworth, P., Jr.; Janda, K. D. *Tetrahedron* **2005**, *61*, 12140.

142. Minati, L.; Biffis, A. *Chem. Commun.* **2005**, 1034.

143. Biffis, A.; Cunial, S.; Spontoni, P.; Prati, L. *J. Catal.* **2007**, *251*, 1.

144. Beletskaya, I. P.; Tarasenko, E. A.; Khokhlov, A. R.; Tyurin, V. S. *Russ. J. Org. Chem.* **2007**, *43*, 1733.

145. Beletskaya, I. P.; Khokhlov, A. R.; Tarasenko, E. A.; Tyurin, V. S. *J. Organomet. Chem.* **2007**, *692*, 4402.

146. Wolfson, A.; Vankelecom, I. F. J.; Jacobs, P. A. *Tetrahedron Lett.* **2003**, *44*, 1195.

147. Zheng, X.; Jones, C. W.; Weck, M. *J. Am. Chem. Soc.* **2007**, *129*, 1105.

148. Park, B. D.; Lee, H. I.; Ryoo, S. J.; Lee, Y. S. *Tetrahedron Lett.***1997**, *38*, 591.

149. Adams, J. H.; Cook, R. M.; Hudson, D.; Jammalamadaka, V.; Lyttle, M. H.; Songster, M. F. *J. Org. Chem.* **1998**, *63*, 3706.

150. Gooding, O. W.; Baudart, S.; Deegan, T. L.; Heisler, K.; Labadie, J. W.; Newcomb, W. S.; Porco, J. A., Jr.; van Eikeren, P. *J. Comb. Chem.* **1999**, *1*, 113.

151. Kim, H.; Cho, J. K.; Aimoto, S.; Lee, Y. S. *Org. Lett.* **2006**, *8*, 1149.

152. Shin, D. S.; Kim, Y. G.; Kim, E. M.; Kim, M.; Park, H.Y.; Kim, J.H.; Lee, B. S.; Kim, B. G.; Lee, Y. S. *J. Comb. Chem.* **2008**, *10*, 20.

153. Kobayashi, Y.; Tanaka, D.; Danjo, H.; Uozumi, Y. *Adv. Synth. Catal.* **2006**, *348*, 1561.

154. Uozumi, Y.; Nakao, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 194.

155. Kita, R.; Svec, F.; Fre´chet, J. M. J. *J. Comb. Chem.* **2001**, *3*, 564.

156. Wan, Y.; Huang, W.; Wang, Z.; Zhu, X. X. *Polymer* **2004**, *45*, 71.

157. Gauthier, M. A.; Luo, J.; Calvet, D.; Ni, C.; Zhu, X. X.; Garon, M.; Buschmann, M. D. *Polymer* **2004**, *45*, 8201.

158. Wang, Z.; Luo, J.; Zhu, X. X.; Jin, S.; Tomaszewski, M. J. *J. Comb. Chem.* **2004**, *6*, 961.

159. Luo, J.; Pardin, C.; Zhu, X. X.; Lubell, W. D. *J. Comb. Chem.* **2007**, *9*, 582.

160. Grøtli, M.; Gotfredsen, C. H.; Rademann, J.; Buchardt, J.; Clark, A. J.; Duus, J. Ø.; Meldal, M. *J. Comb. Chem* **2000**, *2*, 108.

161. Miranda, L. P.; Lubell, W. D.; Halkes, K. M.; Groth, T.; Grøtli, M.; Rademann, J.; Gotfredsen, C. H.; Meldal, M. *J. Comb. Chem.* **2002**, *4*, 523.

162. Benko, A.; Prince, M.; Price, B. J.; Kaltcheva, N. T.; Geissinger, P.; Schwabacher, A. W. *J. Comb. Chem.* **2006**, *8*, 221.

163. Garcı´a-Martı´n, F.; Quintanar-Audelo, M.; Garcı´a-Ramos, Y.; Cruz, L. J.; Gravel, C.; Furic, R.; Co^te´, S.; Tulla-Puche, J.; Albericio, F. *J. Comb. Chem.* **2006**, *8*, 213.

164. Sunder, A.; Hanselmann, R.; Frey, H.; Mu¨lhaupt, R. *Macromolecules* **1999**, *32*, 4240.

165. Haag, R.; Stumbe´, J. F.; Sunder, A.; Frey, H.; Hebel, A. *Macromolecules* **2000**, *33*, 8158.

166. Garcia-Bernabe´, A.; Dominguez-Espinosa, G.; Dı´az-Calleja, R.; Riande, E.; Haag, R. *J. Chem. Phys.* **2007**, *127*, 124904

167. Frey, H.; Haag, R. *Rev. Mol. Biotechnol.* **2002**, *90*, 257.

168. Roller, S.; Siegers, C.; Haag, R. *Tetrahedron* **2004**, *60*, 8711.

169. Koc¸, F.; Wyszogrodzka, M.; Eilbracht, P.; Haag, R. *J. Org. Chem.* **2005**, *70*, 2021.

170. Hebel, A.; Haag, R. *J. Org. Chem.* **2002**, *67*, 9452.

171. Roller, S.; Zhou, H.; Haag, R. *Mol. Diversity* **2005**, *9*, 305.

172. Hajji, C.; Roller, S.; Beigi, M.; Liese, A.; Haag, R. *Adv. Synth. Catal.* **2006**, *348*, 1760.

173. Beigi, M.; Haag, R.; Liese, A. *Adv. Synth. Catal.* **2008**, *350*, 919.

174. Beigi, M.; Roller, S.; Haag, R.; Liese, A. *Eur. J. Org. Chem.* **2008**, 2135.

175. Roller, S.; Tu¨rk, H.; Stumbe´, J.-F.; Rapp, W.; Haag, R. *J. Comb. Chem.* **2006**, *8*, 350.

176. Cavalli, G.; Shooter, A. G.; Pears, D. A.; Steinke, J. H. G. *J. Comb.Chem.* **2003**, *5*, 637.

177. Cavalli, G.; Shooter, A. G.; Pears, D. A.; Wellings, D. A.; Gulzar, S.; Steinke, J. H. G. *J. Comb. Chem.* **2007**, *9*, 1012.

178. Shimomura, O.; Lee, B. S.; Meth, S.; Suzuki, H.; Mahajan, S.; Nomura, R.; Janda, K. D. *Tetrahedron* **2005**, *61*, 12160.

179. Rademann, J.; Barth, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 2975.

180. Roice, M.; Christensen, S. F.; Meldal, M. *Chem.Eur. J.* **2004**, *10*, 4407.

181. Haimov, A.; Cohen, H.; Neumann, R. *J. Am. Chem. Soc.* **2004**, *125*, 11762.

182. Kotre, T.; Nuyken, O.; Weberskirch, R. *Macromol. Rapid Commun.* **2002**, *23*, 871.

183. Zarka, M. T.; Nuyken, O.; Weberskirch, R. *Chem.Eur. J.* **2003**, *9*, 3228.

184. Krause, J. O.; Zarka, M. T.; Anders, U.; Weberskirch, R.; Nuyken, O.; Buchmeiser, M. R. *Angew. Chem., Int. Ed.* **2003**, *42*, 5965.

185. Zarka, M. T.; Bortenschlager, M.; Wurst, K.; Nuyken, O.; Weberskirch, R. *Organometallics* **2004**, *23*, 4817.

186. Rossbach, B. M.; Leopold, K.; Weberskirch, R. *Angew. Chem., Int. Ed.* **2006**, *45*, 1309.

187. Schonfelder, D.; Fischer, K.; Schmidt, M.; Nuyken, O.; Weberskirch, R. *Macromolecules* **2005**, *38*, 254.

188. Schonfelder, D.; Nuyken, O.; Weberskirch, R. *J. Organomet. Chem.* **2005**, *690*, 4648.

189. Bortenschlager, M.; Scho¨llhorn, N.; Wittmann, A.; Weberskirch, R. *Chem. Eur. J.* **2007**, *13*, 520.

190. Moore, J. S.; Stupp, S. I. *Macromolecules* **1986**, *19*, 1815.

191. Yamada, Y. M. A.; Uozumi, Y. *Org. Lett.* **2006**, *8*, 1375.

192. Yamada, Y. M. A.; Uozumi, Y. *Tetrahedron* **2007**, *63*, 8492.

193. Yamada, Y. M. A.; Guo, H.; Uozumi, Y. *Org. Lett.* **2007**, *9*, 1501.

194. Seyferth, D. *Inorganic and Organometallic Polymers, ACS Symposium Series*, **1988**, *360*, 21.

195. Birot, M.; Pillot, J.P.; Dunogues, J. *Chem. Rev.* **1995**, *95*, 1443.

196. Interrante, L.V.; Rushkin, I.; Shen, Q. *Appl. Organometal. Chem.* **1998**, *12*, 695.

197. Ganicz, T.; Stanczyk, W. A.; Chmielecka, J.; Kowalski, J. *Polym. Int.*, **2009**, *58*, 248.

198. Greenberg, S.; Clendenning, S. B.; Liu, K.; Manners, I. *Macromolecules*, **2005**, *38*, 2023.

199. Ganicz, T.; Stanczyk, W. A.; Gladkova, N. K.; Śledzińska, I. *Macromolecules*, **2000**, *33*, 289.

200. Wang, X.; Yuan, Y.; Graiver, D.; Cabasso, I. *Macromolecules*, **2007,** *40*, 3939.

201. Lee, Y. J.; Lee, J. H.; Kim, S. R.; Kwon, W. T.; Klepeis, J. P.; Teat, S. J.; Kim, Y. H. *J. Mater. Sci.*, **2010**, *45*, 1025.

202. Schilling, C. L.; Hudson, C. O.; William, T. C. US Patent, 4,472,591, **1984**.

203. Krawiec, P.; Kockrick, E.; Borchardt, L.; Geiger, D.; Corma, A.; Kaskel, S. *J. Phys. Chem, C.*, **2009**, *113*, 7755.

204. Oyamada, H.; Akiyama, R.; Hagio, H.; Naito, T.; Kobayashi, S. *Chem. Commun.*, **2006**, *31*, 5609.

205. Miller, R. D.; Michl, J. *Chem. Rev*. **1989**, *89*, 1359.

206. West, R. *J. Organomet. Chem*. **1986**, *300*, 327.

207. Gahimer, T.; Welsh, W. J. *Polymer* **1996**, *37*, 1815.

208. Oka, K.; Fujiue, N.; Nakanishi, S.; Takata, T.; West, R.; Dohmaru, T. *J. Organomet. Chem.* **2000**, *611*, 45.

209. West, R.; Menescal, R.; Asuke, T.; Eveland, J. *J. Inorg. Organomet.Polym.* **1992**, *2*, 29.

210. Naito, M.; Fujiki, M. *Soft Mater.* **2008**, *4*, 211.

211. Reuss, V. S.; Frey, H. *Macromolecules* **2010**, *43*, 8462.

212. Frey, H.; Moller, M.; Turetskii, A.; Lotz, B.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 5498.

213. Fujiki, M. *Macromol. Rapid Commun*. **2001**, *22*, 539.

214. Ohira, A.; Okoshi, K.; Fujiki, M.; Kunitake, M.; Naito, M.; Hagihara, T. *Adv. Mater.* **2004**, *16*, 1645.

215. Kipping, F. S. *J. Chem. Soc.* **1924**, *125*, 2291.

216. Burkhard, C. *J. Am. Chem. Soc.* **1949**, *71*, 963. Burkhard: C. U.S. Patent 2,554,976, **1951**.

217. Wesson, J. P.; Williams, T. C. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18,* 959.

218. Koe, J. *Polym. Int.* **2009**, *58*, 255.

219. Seki, T.; Tamaki, T.; Ueno, K. *Macromolecules* **1992**, *25*, 3825.

220. Horiguchi, R.; Onishi, Y.; Hayase, S. *Macromolecules* **1988**, *21*, 304.

221. Schwegler, L. A.; Meyer-Pundsack, C.; Moller, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2306.

222. Cao, F.; Kim, D.; Li, X. *J. Mater. Chem.* **2002**, *12*, 1213.

223. Choi, S. H.; Youn, D. Y.; Jo, S. M.; Oh, S. G. *ACS Appl. Mater. Interfaces* **2011,** *3*, 1385.

224. Yu, Z.; Fang, Y.; Huang, M.; Li, R.; Zhan, J.; Zhou, C.; He, G.; Xia, H. *Polym. Adv. Technol.,* **2011**, doi: 10.1002/pat.1777.

225. Zeigler, J. M.; Fearon, F. W. G. '*Silicon-Based Polymer Science A Comprehensive Resource*, *Advances in Chemistry Series 224"* **1990**, Washington, DC, American Chemical Society.

226. Schilling, C. L.; Hudson, C. O.; William, T. C.; Wesson, J. P. US Patent, 4,497,787, **1985**.

227. Iseki, T.; Narisawa, M.; Katase, Y.; Oka, K.; Dohmaru, T.; Okamura, K. *Chem, Mater.*, **2001**, *13*, 4163.

228. Tsirlin, A.M.; Shcherbakova, G.I.; Florina, E.K.; Popova, N.A.; Gubin, S.P.; Moroz, E.M.; Riedel, R**.;** Kroke, E.; Steen, M. *J. Eur. Ceram. Soc.* **2002,** *22*, 2577.

229. Krawiec, P.; Kockrick, E.; Borchardt, L.; Geiger, D.; Corma, A.; Kaskel, S. *J. Phys. Chem, C.*, **2009**, *113*, 7755.

230. Yajima, S.; Hayashi, J.; Omori, M. Japanese Appl. **75** 50,529, **1975**; *Chem. Abstr.* **1977,** 86,45291.

231. Nicalon from Nippon Carbon Co. Ltd., 2-6-1, Hatbochori, Chuko, Tokyo 104, Japan.

232. Verbeek, W.; Winter, G. German Patent 2,236,078, **1974**; *Chem. Abstr.* **1974,** 81, 50911.

233. Yajima, S.; Hayashi, J.; Omori, M.; Okamura, K. *Nature* **1976**, 261. 683.

234. Yajima, S.; Hasegawa, Y.; Hayashi, J.; Iimura, M. *J. Mater. Sci.* **1978**,13,2569

235. Smith, T. L., Jr. U.S. Patent 4,631,179, **1986;** *Chem. Abstr.* **1987**, 106, 106920**.**

236. Wu, H. J.; Interrante, L. V. *Polym. Prepr.* **1992,** *33*, 210.

237. Kriner, W. A. *J. Org. Chem.* **1964***, 29*, 1601.

238. Bacque, E.; Pillot, J. P.; Birot, M.; Dunogubs, J. *Macromolecules* **1988***, 21,* 34.

239. Seyferth, D.; Lang, H. *Organometallics* **1991,** *10,* 551.

240. Zhou, S. Q.; Manuel, G.; Weber, W. P. *Macromolecules* **1990,** *23*, 1583.

241. Ko, Y. H.; Weber, W. P. *Polym. Bull.* **1991**, *26*, 487.

242. Zhou, S. Q.; Weber, W. P. *Macromolecules* **1992***, 25,* 1639.

243. Theurig, M.; Sargeant, S. J.; Manuel, G.; Weber, W. P. *Macromolecules* **1992***, 25*, 3834

244. Shin Etsu Chemical Industry, Japanese Patent 58 67,729, **1983;** *Chem. Abstr.* **1983,** 99, 176478.

245. Schilling, C. L. Jr,'Wesson, J. P.; Williams, T. C. *Am. Ceram. Soc. Bull.* **1983***, 62,* 912.

246. Schilling, C. L., Jr.; Williams, T. C. U.S. Patent 4,472,591, **1984**; *Chem. Abstr.* **1985**, 102, 9014.

247. Whitmarsh, C. R; Interrante, L. V. *Organometallics* **1991***, 10,* 1336.

248. Whitmarsh, C. R.; Interrante, L. V. US. Patent 5,153,295, **1992**; *Chem. Abstr.* **1993**, 118, 10694

249. Dvornic, P. R.; Owen, M. J. *Silicon-Containing Dendritic Polymers: Advances in Silicon Science,* **2009**, *2*, USA, Springer

250. Seyferth, D.; Sobon, C. A.; Borm, J. *New J. Chem*. **1989**, *14*, 545.

251. Pillot, J.-P.; Bacque, E.; Dunogues, J.; Olry, P. German Patent 3,717,450, **1987;** *Chem. Abstr.* **1988,** 108, 151208.

252. Sartori, P.; Van Aefferden, B.; Habel, W. German Patent 3,841,348, **1990;** *Chem. Abstr.* **1991**, 114, 63022.

253. Ijadi-Maghsoodi, S.; Barton, T. J. *Macromolecules* **1990**, *23*, 4485.

254. Corriu, R.; Gerbier, P.; Guerin, C.; Henner, B.; Fourcade, R. *J. Organomet. Chem.* **1993**, *449*, 111.

255. Corriu, R.; Boury, B.; Carpenter, L. European Patent Appl. 300,862, **1989;** *Chem. Abstr.* **1989**, 111, 8038.

256. Boury, B.; Corriu, R.; Leclercq, D.; Mutin, P.; Planeix, 3. M.; Vioux, A. *Organometallics* **1991***, 10,* 1457.

257. Schilling, C. L., Jr.; Williams, T. C. European Patent Appl. 139,257, **1985;** *Chem. Abstr.* **1986**, 104, 6568.

258. Schilling, C. L. Jr,'Wesson, J. P.; Williams, T. C. *Am. Ceram. Soc. Bull.* **1983**, *62*, 912.

259. Peterson, W. R., Jr.; Arkles, B. C. U.S. Patent 4,276,424, **1981**.

260. Brown-Wensley, K. A.; Sinclair, R. A. U.S. Patent 4,537,942, **1985**.

261. Brown-Wensley, K. A.; Sinclair, R. A. U.S. Patent 4,704,444, 1987.

262. Noireaux, P.; Jamet, J.; Parlier, M.; Bacos, M-P. U.S. Patent 5,091,485, **1992**.

263. Hang, M.; Fang, Y.; Li, R.; Huang, T.; Yu, Z.; Xia, H. *J. Appl. Polym. Sci.,* **2009,** *113*, 1611.

264. Chan, W.Y.; Clendenning, S. B.; Berenbaum, A.; Lough, A. J.; Aouba, S.; Ruda, H. E. Manners, I. *J Am Chem Soc*. **2005**, *127*, 1765.

265. Oyamada, H.; Akiyama, R.; Hagio, H.; Naito, T.; Kobayashi, S. *Chem. Commun.* **2006**, *41*, 4297.

266. Rushkin, I. L.; Shen, Q.; Lehman, S. E.; Interrante, L. V. *Macromolecules*, **1997**, *30*, 3141.

267. Vipin, A. *Studies on Polymer Supported Transition Metal Catalysts* Ph.D. thesis, University of Kerala, Thiruvananthapuram, **2001** .

268. Ly, H. Q.; Day, R. J. *J. Mater. Sci.* **2001**, *36*, 4037

269. Astruc, D.; Boisselier, E.; Ornelas, C. *Chem. Rev.* **2010**, *110,* 1857.

270. Lakshmi S. K.; Ramesh, R.; Murthy V. S. N. M.; Nithyanandhan, J; Jayaraman, N.; Ramamurthy, V. *J. Org. Chem.*, **2005**, 70, 5062.

271. Tomalia, D. A.; Taylor, A. N.; Goddard, W. A., III *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.

272. Ardoin, N.; Astruc, D. *Bull. Soc. Chim. Fr.* **1995**, *132*, 875.

273. Buhleier, E. W.; Wehner, W.; Vogtle, F. *Synthesis* **1978**, 155.

274. Denkewalter, R. G.; Kolc, J.; Lukasavage, W. J. U.S. Pat. 4,289,872, **1981**.

275. Aharoni, S. M.; Crosby, C. R, III.; Walsh, E. K. *Macromolecules* **1982**, *15*, 1093.

276. Newkome, G. R.; Yao, Z. Q.; Baker, G. R.; Gupta, K. *J. Org. Chem.* **1985**, *50*, 2003.

277. Tomalia, D. A.; Baker, H.; Dewald, J. R.; Hall, M.; Kallos, G.; Martin, S.; Roeck, J.; Ryder, J.; Smith, P. *Macromolecules* **1986**, *19*, 2466.

278. Fre´chet, J. M. J. *Science* **1994**, *263*, 1710.

279. Fre´chet, J. M. J.; Hawker, C. J.; Gitsov, I.; Leon, J. W. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 1399.

280. Moore, J. S. *Acc. Chem. Res*. **1997**, *30*, 402.

281. Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681.

282. Jayaraman, N.; Negopodiev, S. A.; Stoddart, J. F. *Chem. Eur. J.* **1997**, *3*, 1193.

283. Balzani, V.; Campana, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26.

284. Smith, D. K.; Diederich, F. *Chem. Eur. J.* **1998**, *4*, 1353.

285. Archut, A.; Vo¨gtle, F. *Chem. Soc. Rev*. **1998**, *27*, 233.

286. Chow, H.-F.; Mong, T. K.-K.; Nongrum, M. F.; Wan, C. W. *Tetrahedron* **1998**, *54*, 8543.

287. Gorman, C. *Adv. Mater.* **1997**, *19,* 1117.

288. Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665.

289. Newkome, G. R.; He, E.; Moorefield, C. N. *Chem. Rev.* **1999**, *99*, 1689.

290. Bryce, M. R.; Devonport, W.; Moore, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1761.

291. Fisher, F.; Vo¨gtle, F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 885.

292. Majoral, J. P.; Caminade, A. M. *Chem. Rev.* **1999**, *99*, 845.

293. Tomalia, D. A.; Dvornic, P. R. *Nature* **1994**, *372*, 617.

294. Herrmann, W. A.; Cornils, B. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1047.

295. Halm, C.; Kurth, M. *Angew. Chem., Int. Ed. Engl*. **1998**, *37*, 510.

296. Kobayashi, S.; Nogayama, S. *J. Am. Chem. Soc*. **1998**, *120*, 2985.

297. Mehnert, C. P.; Weaver, D. W.; Ying, J. Y. *J. Am. Chem. Soc*. **1998**, *120*, 12289.

298. Annis, D. A.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1999**, *121*, 707.

299. Corma, A. *Chem. Rev*. **1997**, *97*, 2373.

300. Boury, B.; Corriu, R. J. P.; Nunez, R. *Chem. Mater.* **1998**, *10*, 1795.

301. Tsukruk, V. V. *Adv. Mater.***1998**, *10*, 253.

302. Kriesel, J, Tilley, T. D. *Chem. Mater*. **1999**, *11*, 1190.

303. Liu, M.; Kono, K.; Frechet, J. *J. Cont. Rel.* **2000**, *65*, 121.

304. Stevelmens, S., Hest, J. C. M., Jansen, J. F. G. A., Boxtel, D. A. F. J., de Bravander-van den, B., Miejer, E. W. *J Am Chem Soc.* **1996,** *118*, 7398.

305. Gupta, U; Agashe, H.B.; Asthana, A.; Jain, N.K. *Synthesis* **2006**, 7, 155.

306. Thomas, T.P.; Majoros, I.J.; Kotlyar, A.; Kukowska-Latallo, J.F.; Bielinska, A.; Myc, A.; Baker Jr., J.R. *J. Med. Chem.* **2005**, *48,* 3729.Bhadra, D.; Bhadra, S.; Jain, P.; Jain, N.K. *Synthesis* **2002**, *57*, 5.Bhadra, D.; Bhadra, S.; Jain, P.; Jain, N.K. *Synthesis* **2003**, *257*, 111.

309. Khopade, A.J.; Caruso, F.; Tripathi, P.; Nagaich, S.; Jain, N.K. *Int. J. Pharm.* **2002**, *232*, 157.

310. Prajapati, R. N.; Tekade, R. K; Gupta, U.; Gajbhiye, V.; Jain, N. K.; *Synthesis* **2009**, *6*, 940.

311. Chauhan, A.S.; Sridevi, S.; Chalasani, K.B.; Jain, A.K.; Jain, S.K.; Jain, N.K.; Diwan, P.V. *Synthesis* **2003,** *90*, 335.

312. Kukowska-Latallo, J. F.; Candido, K.A.; Cao, Z.; Nigavekar, S.S.; Majoros, I.J.; Thomas, T.P.; Balogh, L.P.; Khan, M.K.; Baker Jr., J.R. *Synthesis* **2005** , *65*, 5317.

313. Quintana, A.; Raczka, E.; Piehler, L.; Lee, I.; Myc, A.; Majoros, I.; Patri, A.K.; Thomas, T.; Mule, J.; Baker Jr. J.R. *Synthesis* **2002**, *19*, 1310.

314. Benaglia, M.; Puglisi, A.; Cozzi, F. *Chem. Rev.*, **2003**, *103*, 3401.

315. Breslow, R. *Science* **1982**, *218*, 532.

316. Li, Y.; Liu, J. H. C.; Witham, C. A.; Huang, W.; Marcus, M. A.; Fakra, S. C.; Alayoglu, P.; Zhu, Z.; Thompson, C. M.; Arjun, A.; Lee, K.; Gross, E.; Dean Toste, F. D.; Somorjai, G. A. *J. Am. Chem. Soc.* **2011**, *133*, 13527.

317. Gladysz, J. A. *Chem. Rev.* **2002**, *102*, 3215.

318. Ley, S. V.; Baxendale, I. R.; Bream, R. N.; Jackson, P. S.; Leach, A. G.; Longbottom, D. A.; Nesi, M.; Scott, J. S.; Storer, R. I.; Taylor, S. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3815.

319. de Miguel, Y. R.; Brule´, E.; Margue, R. C. *J. Chem. Soc., Perkin Trans. 1* **2001**, 3085.

320. Clapham, B.; Reger, T. S.; Janda, K. *Tetrahedron* **2001**, *57*, 4637.

321. Van Heerbeek, R.; Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Chem. Rev.* **2002**, *102*, 3717.

322. Twyman, L. J.; King, A. S. H.; Martin, I. K. *Chem. Soc. Rev.* **2002**, *31*, 69.

323. Dömling, I. Ugi, *Angew. Chem. Intl. Ed.* **2000**, *39*, 3168.

Chapter 2

SYNTHESIS AND CHARACTERIZATION OF POLYCARBOSILANES

Contents

2.1. Introduction

Polycarbosilanes (PCSs), in their broadest definition, are organosilicon polymers whose back bone is composed of appropriately substituted silicon atoms and difunctional organic groups which bridge the silicon atoms[1,2]. Polycarbosilanes are organic-inorganic hybrid polymers which have both Si and C in their back bone structure; they have been of exacting significance as potential precursor to SiC[3-10], a ceramic material which is of considerable technological importance due to its high thermal, chemical and oxidative stability, as well as for its electrical (semiconductor) and mechanical (high hardness, shock resistance, strength etc.) properties[11, 12]. It is not hard to envision variety of possible application that are opening up for these hybrid polymers in the areas such as nanotechnology, surface science, bio-medicine, catalysis, electrochemistry, liquid crystals, new ceramic materials, organic hybrid and nanocomposites etc[14-22]. Many of these applications play dominant roles in the development of science in the twenty first century, and we have no doubt that silicon will occupy a prominent position in all of them as well.

Various routes[7-10] to polycarbosilanes were put forward by different scientific groups. Several investigators[20-22] have explored the use of alkali metals for the reductive-coupling of silanes. Appropriate route for the synthesis of partially cross-linked structure into the polycarbosilane have to be selected, to make the further functionalization easy.

The preparation of polycarbosilanes by reacting chlorosilanes with unsaturated compounds in the presence of metallic reducing agents has been adopted. This route proves to be moderately simple way to prepare cross-linked polycarbosilane.

The polycondensation of chlorosilanes and vinyl silanes to prepare polycarbosilanes have been carried out. The chlorosilane monomer on reaction in the presence of a metallic reducing agent such as sodium leads to the formation of polymer, by Wurtz type coupling[28]. The polysilane on thermal rearrangement gives polycarbosilane. The transformation proceeds through Kumada rearrangement[10,23]; which is an insertion of methylene group into a Si-Si bond. Wurtz coupling between chlorosilanes and unsaturated compounds leads to the formation of polycarbosilanes. Wurtz type coupling reaction, which makes use of alkali metals, can generally lead to appreciable Si-Si and C-C bonding, in addition to Si-C bonding, and extensive cross-linking.

The reactivity of Si-X (where X= Cl, OR or H) is very high[24], the nucleophilic reactions can direct to the formation of hyperbranched polycarbosilane back bone. This methodology has also been used widely to attach side chains and to modify the structure of the originally obtained polycarbosilane through reaction with Si-Cl or Si-OR groups on the polymer back bone. Consequently this methodology has been, and is expected to continue to be, an important component of the chemical tool kit that is available for the preparation and effective utilization of this important class of organosilicon polymers[19,25,26].

In this chapter, preparation of polycarbosilanes is described. Polycarbosilanes were synthesized from corresponding monomers, trichloromethylsilane, chlorodimethylvinylsilane, diethoxymethylvinylsilane and trimethoxyvinylsilane. Homopolymers with trichloromethylsilane, diethoxymethylvinylsilane and copolymers with trichloromethylsilane in combination with chlorodimethylvinylsilane, diethoxymethylvinylsilane, trimethoxyvinylsilane were synthesized. In total five polymers were prepared. The preparation involves the Wurtz-type coupling reaction of monomer molecules in the presence of metallic sodium. The synthesized polymers were analysed using various spectral and chemical methods.

2.2. Results and Discussion

2.2.1. Preparation of polycarbosilanes

Trichloromethylsilane, chlorodimethylvinylsilane, diethoxymethylvinylsilane and trimethoxyvinylsilane were selected as the monomers to synthesise polycarbosilanes.

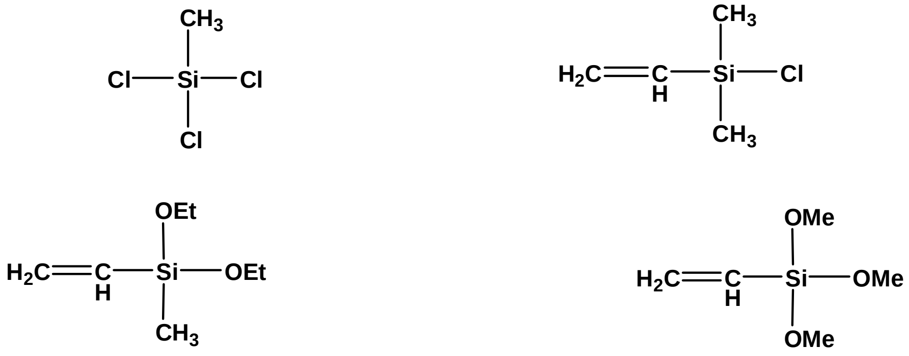


Figure 1: Monomers

The monomers were selected with altered functionality, so as to compare the capability of the monomer to crosslink with varying functional groups.

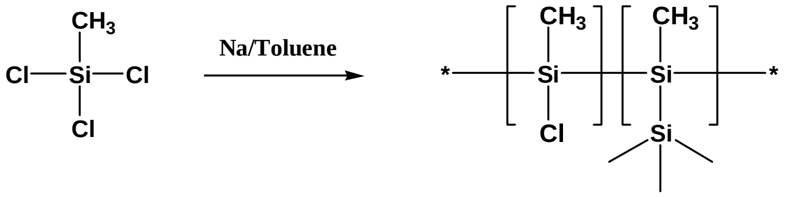
2.2.2. Polycarbosilane from Trichloromethylsilane (PCS 1)

PCS 1 was prepared by two steps,

Former step is the synthesis of polysilane[28]. Polysilanes are generally synthesized by the Wurtz-type reductive-coupling of the corresponding chlorosilane using sodium metal in a high boiling solvent such as toluene. Second step is the thermolysis of polysilane to polycarbosilane.

2.2.2.1. Preparation of polysilane (PMS)

Polysilane was prepared by the Wurtz type coupling of trichloromethylsilane in the presence of metallic sodium in toluene at 100°C. The monomer to sodium metal ratio was 1:1. The reaction was done under N_2 atmosphere.



Scheme 1: Preparation of polysilane

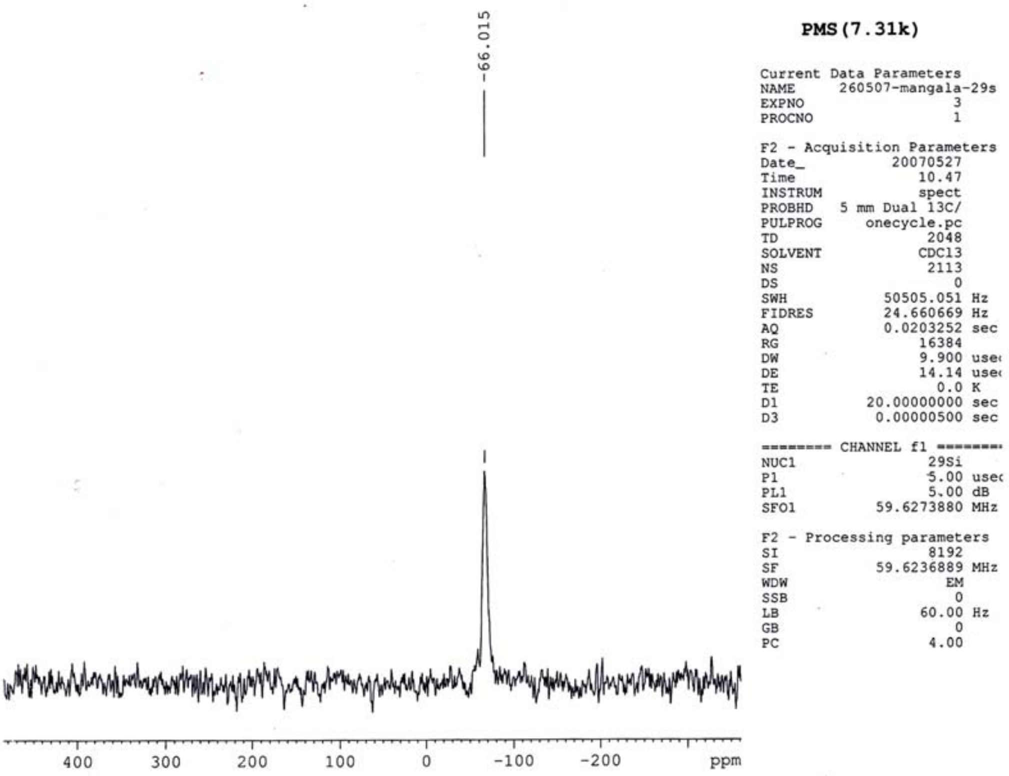
The polysilane obtained was a gelatinous liquid which was soluble in toluene and a white solid which was insoluble in all solvents. The molecular weight was determined for liquid fraction by GPC technique. A pale yellow liquid oligomer of molecular weight Mn = 544, Mw =865 from GPC using polystyrene as standard was obtained. The liquid fraction was discarded.

The insoluble polysilane was analysed with UV-DRS, FT-IR spectroscopy, ^{13}C NMR spectroscopy and ^{29}Si NMR spectroscopy.

UV absorption spectra are very important for the analysis of σ conjugation systems along the Si-Si back bones. The relationship between these spectra and linear polysilane and oligosilane structures have been investigated both theoretically and experimentally. It was found that the UV absorption band of the σ- σ^* transition shows a red-shift, which increases with the length of the linear permethylated Si-Si chains both in polysilanes and in their shorter oligomers. This shift, however, has a limit at about 296 nm, which corresponds to that of the octadecasilane, $Si_{18}Me_{36}$, unit and if the number of silicon atom is increased above 18, no significant further red shift is observed.

Silicon polymers show UV absorption above 200 nm. This result is totally unexpected for a species containing no double bonds. PMS shows an absorbance maximum at 273 nm. This is due to the σ- conjugation of the Si back bone.

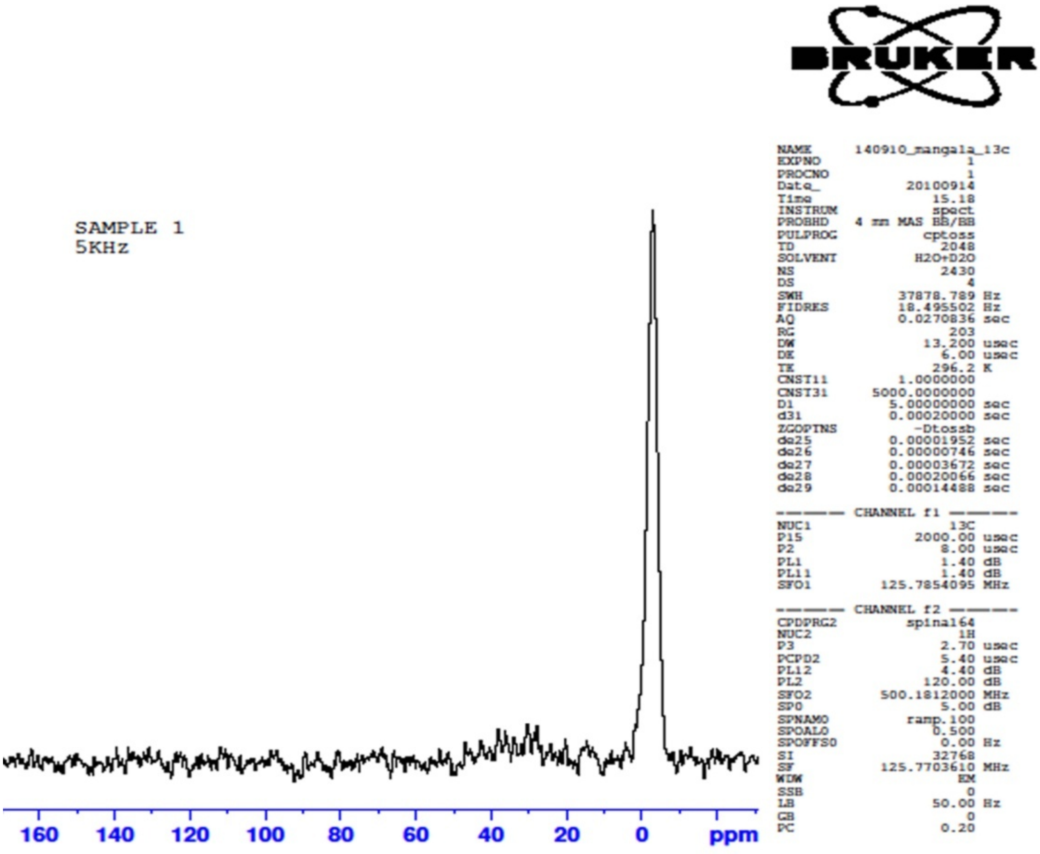
The FT-IR spectrum of the polymer has the corresponding peaks of the polysilane. The spectrum shows a peak at 2952 cm^{-1} which is corresponding to the C-H stretching, peak at 2089 cm^{-1} is due to the Si-H stretching, peak at 1447 cm^{-1} is due to $Si\text{-}CH_3$ stretching, peak at 1252 cm^{-1} corresponds to $Si\text{-}CH_3$ deformation, and 777 cm^{-1} is due to $Si\text{-}CH_3$ wagging. 1045 cm^{-1} due to the Si-O stretching.



```
PMS(7.31k)

Current Data Parameters
NAME      260507-mangala-29s
EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_               20070527
Time                   10.47
INSTRUM                spect
PROBHD     5 mm Dual 13C/
PULPROG         onecycle.pc
TD                      2048
SOLVENT                CDC13
NS                      2113
DS                         0
SWH               50505.051 Hz
FIDRES            24.660669 Hz
AQ                0.0203252 sec
RG                     16384
DW                     9.900 use
DE                     14.14 use
TE                       0.0 K
D1              20.00000000 sec
D3               0.00000500 sec

======== CHANNEL f1 =======
NUC1                    29Si
P1                      5.00 usec
PL1                     5.00 dB
SFO1            59.6273880 MHz

F2 - Processing parameters
SI                      8192
SF              59.6236889 MHz
WDW                       EM
SSB                        0
LB                     60.00 Hz
GB                         0
PC                      4.00
```

Figure 2: ^{29}Si NMR spectrum of PMS

^{29}Si NMR spectrum of PMS is shown in Figure 2. Chemical shifts are based on tetramethylsilane as the internal standard. In the spectrum, the peak around -66.01 ppm was assigned to be due to the resonance of Silicon in (CH_3)*Si*Si unit (branching unit). A small peak in close proximity to it around -60 ppm is corresponding to the (CH_3)Cl*Si*Si_2 unit (linear unit). The branching unit was formed by the elimination of Cl atom from the Si-Cl groups during Wurtz coupling.



```
NAME        140910_mangala_13c
EXPNO                        1
PROCNO                       1
Date_                 20100914
Time                     15.18
INSTRUM                  spect
PROBHD      4 mm MAS BB/BB
PULPROG                 cptoss
TD                        2048
SOLVENT                H2O+D2O
NS                        2430
DS                           4
SWH                  37878.789 Hz
FIDRES               18.495502 Hz
AQ                   0.0270836 sec
RG                         203
DW                      13.200 usec
DE                        6.00 usec
TE                       296.2 K
CNST11               1.0000000
CNST31            5000.0000000
D1                  5.00000000 sec
d31                 0.00020000 sec
ZGOPTNS                -Dtossb
de25                0.00001952 sec
de26                0.00000746 sec
de27                0.00003672 sec
de28                0.00020066 sec
de29                0.00014488 sec

======== CHANNEL f1 ========
NUC1                       13C
P15                    2000.00 usec
P2                        8.00 usec
PL1                       1.40 dB
PL11                      1.40 dB
SFO1               125.7854095 MHz

======== CHANNEL f2 ========
CPDPRG2              spinal64
NUC2                        1H
P3                        2.70 usec
PCPD2                     5.40 usec
PL12                      4.40 dB
PL2                     120.00 dB
SFO2               500.1812000 MHz
SP0                       5.00 dB
SPNAM0                ramp.100
SPOAL0                   0.500
SPOFFS0                   0.00 Hz
SI                       32768
SF                 125.7703610 MHz
WDW                         EM
SSB                          0
LB                       50.00 Hz
GB                           0
PC                        0.20
```

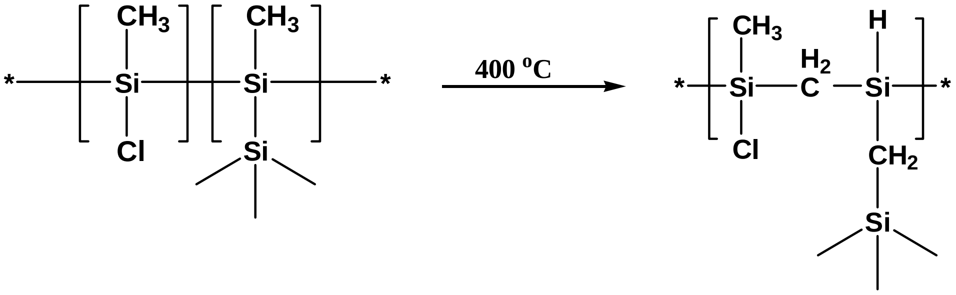
Figure 3: ^{13}C NMR spectrum of PMS

The solid state ^{13}C NMR spectrum of PMS (shown in figure 3) exhibits only one resonance signal centered at -2.93 ppm, which can be assigned to $SiSiCH_3$. The ^{13}C NMR spectrum of PMS indicates that it has only single sort of carbon atom and also that it is attached to the Si atom.

2.2.2.2. Thermolysis of polysilane

The polysilane was heated upto 400°C in a muffle furnace for 4h. The polysilane has undergone Kumada rearrangement and gave crosslinked polycarbosilane.

The polycarbosilane was characterised with TG-DTA, X-ray Diffraction analysis, Surface area analysis, FT-IR spectroscopy, ^{13}C NMR spectroscopy and ^{29}Si NMR spectroscopy.



Scheme 2: Preparation of PCS 1

The FT-IR spectrum of PCS 1 has the corresponding peaks of the polycarbosilane. Peaks at 1441, 1253, 772 cm^{-1} are clearly seen in the spectrum which corresponds to the $CHSiCH_3$ and SiC. The spectrum shows peaks at 2948 and 2899 cm^{-1} which corresponds to the C-H stretching and 1038 cm^{-1} is due to CH_2 wagging in Si-CH_2-Si bond.

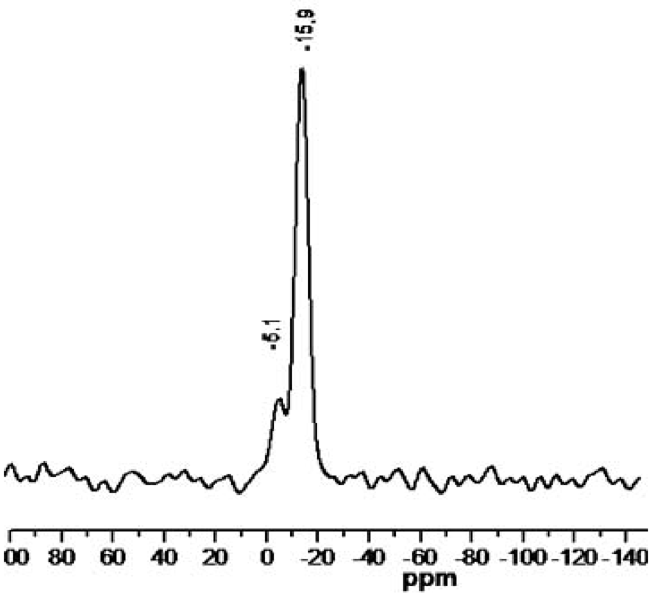


Figure 4: ^{29}Si NMR spectrum of PCS 1

^{29}Si CP-MAS NMR spectrum of the PCS 1 is shown in figure 4. Spectrum gives a clear idea about the structure of the polycarbosilane. The spectrum shows a single peak. Peak around -15ppm corresponds to $CH_3\mathit{Si}(CH_2)_2$ linkage. The broad signal centered at -15.9 ppm is attributed to the overlapped signals of $(CH_2)_2Si(CH_2)_2$ units also which have a resonance around -5.1 ppm.

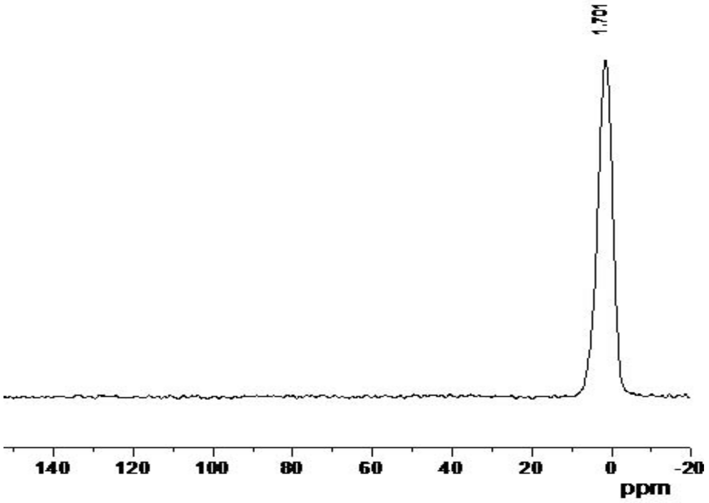
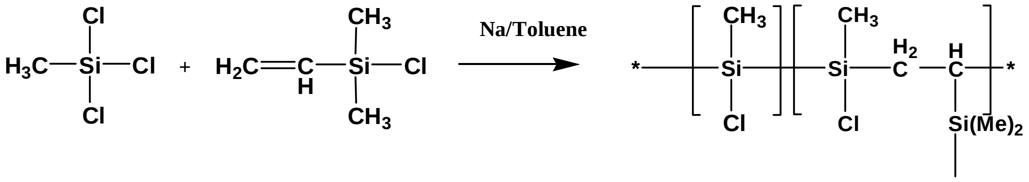


Figure 5: ^{13}C NMR spectrum of PCS 1

The ^{13}C NMR spectrum of PCS 1 shows a broad single peak around 1.70 ppm. The peak around -2.93 ppm of PMS has been shifted to 1.70 which points towards the conversion of polysilane to polycarbosilane. The peak indicates the resonance of carbon atom in Si-CH_2-Si linkage and the absence of carbon atom attached to Si-Si bond.

2.2.3. Preparation of polycarbosilane from trichloromethylsilane and chlorodimethylvinylsilane (PCS 2)

Polycarbosilane was prepared by the sodium metal mediated copolymerization of chlorodimethylvinylsilane with trichloromethylsilane in a ratio of 1:1. The reactions were done in toluene, as solvent and nitrogen atmosphere. The solid polycarbosilane, which was not soluble in any solvents, was characterised by TG-DTA, XRD analysis, FT-IR spectroscopy, ^{13}C NMR spectroscopy and ^{29}Si NMR spectroscopy.

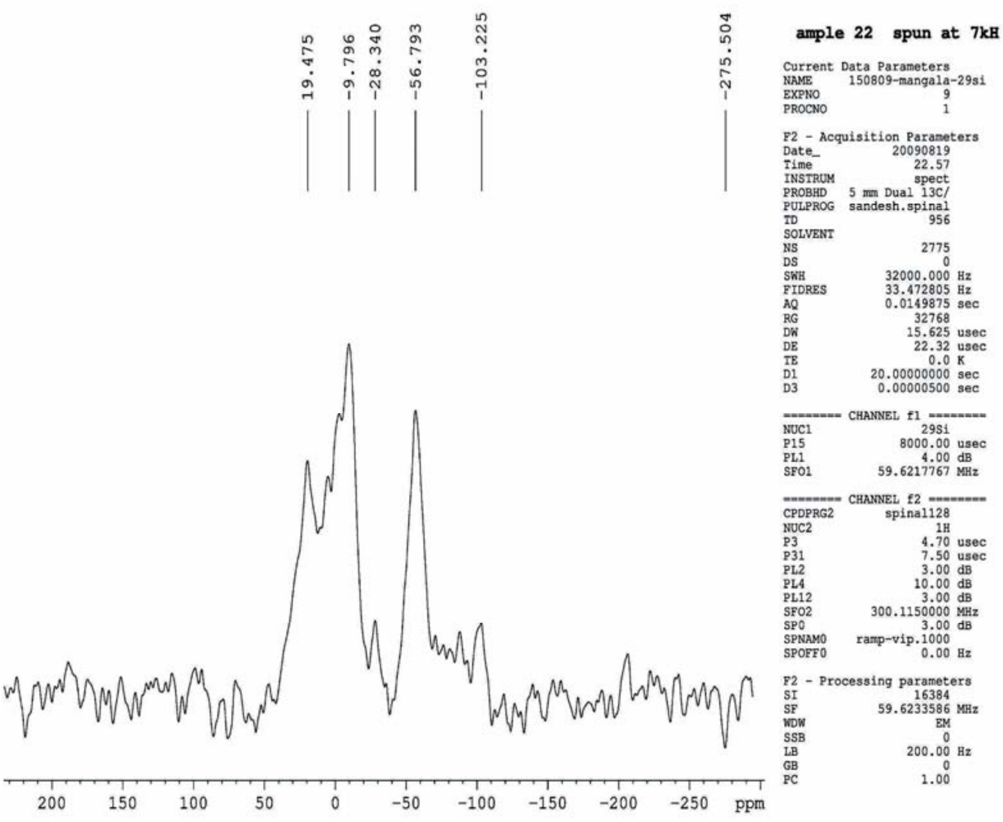


Scheme 3: Preparation of PCS 2

A pale yellow liquid oligomer of molecular weight Mn = 544, Mw =865 from GPC using polystyrene as standard and a white solid polymer was obtained. The liquid fraction was discarded.

The FT-IR spectrum of PCS 2 has the corresponding peaks of the polycarbosilane. Peaks at 1514, 1231, 800 cm^{-1} are clearly seen in the spectrum which correspond to the $CHSiCH_3$ and SiC. The spectrum shows a peak at 2828 cm^{-1} which corresponds to the C-H stretching, peak at 1514 cm^{-1} which is due to Si-CH_3 stretching, 1231 cm^{-1} corresponding to Si-CH_3 deformation, 1038 cm^{-1} due to CH_2 wagging in Si-CH_2-Si bond and 800 cm^{-1} due to Si-CH_3 wagging.

The peaks assigned to Si-O-Si bonds (around 1040 cm^{-1}) are observed in all polymers, since this peak intensified with prolonged air exposure, polymers may have oxidised during the handling and recording processes.



```
ample 22  spun at 7kH

Current Data Parameters
NAME     150809-mangala-29si
EXPNO                      9
PROCNO                     1

F2 - Acquisition Parameters
Date_              20090819
Time                  22.57
INSTRUM               spect
PROBHD   5 mm Dual 13C/
PULPROG  sandesh.spinal
TD                      956
SOLVENT
NS                     2775
DS                        0
SWH            32000.000 Hz
FIDRES         33.472805 Hz
AQ             0.0149875 sec
RG                    32768
DW                15.625 usec
DE                 22.32 usec
TE                   0.0 K
D1           20.00000000 sec
D3            0.00000500 sec

======== CHANNEL f1 ========
NUC1                   29Si
P15              8000.00 usec
PL1                 4.00 dB
SFO1          59.6217767 MHz

======== CHANNEL f2 ========
CPDPRG2           spinal128
NUC2                     1H
P3                  4.70 usec
P31                 7.50 usec
PL2                 3.00 dB
PL4                10.00 dB
PL12                3.00 dB
SFO2         300.1150000 MHz
SP0                 3.00 dB
SPNAM0     ramp-vip.1000
SPOFF0              0.00 Hz

F2 - Processing parameters
SI                    16384
SF            59.6233586 MHz
WDW                      EM
SSB                       0
LB                200.00 Hz
GB                        0
PC                     1.00
```

Figure 6: ^{29}Si CP-MAS NMR spectrum of PCS 2

^{29}Si CP-MAS NMR spectrum of PCS 2 is given in figure 6. Peak around 19.47 ppm corresponds to *Si*-O-Si linkage, which might have resulted due to the oxidation of the pendant group. A peak at -9.79 ppm which corresponds to $(CH_3)_2\mathit{Si}(CH_2)_2$ may be observed due to the side chain polymerization, peaks around -28.34 ppm corresponds to $(CH_2)_2\mathit{Si}Si$ and -56.793 ppm is because of the resonance of *Si*-Si which might be formed by the head to head polymerization of the monomers.

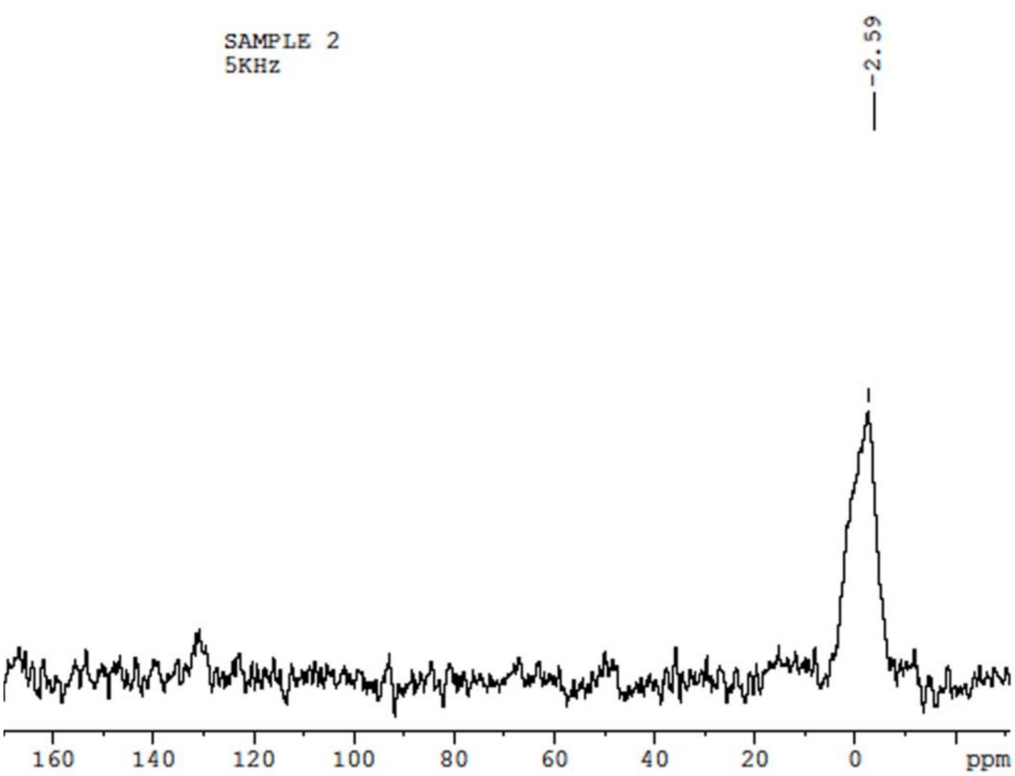
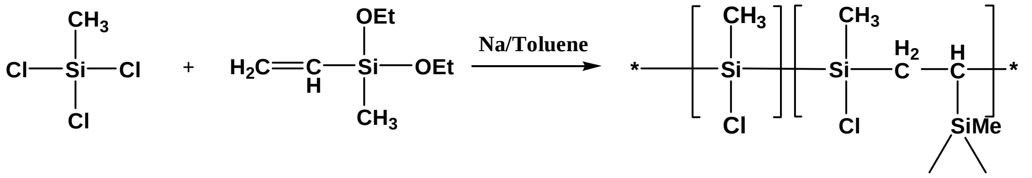


Figure 7: ^{13}C NMR spectrum of PCS 2

The solid state ^{13}C NMR spectrum of PCS2 (shown in figure 7) exhibits only one resonance signal centered at -2.59 ppm, which is a broad signal ranging from +10 ppm to -10 ppm. There is no signal in the vicinity of 120 ppm, which is a sign of the absence of unreacted vinyl group. The signal centered at -2.59 ppm is attributed to the overlapped signals of $SiSiCH_3$ units and $Si\text{-}CH_2$ units, which have the resonance signal around -4.3 ppm and 10.0 ppm respectively.

2.2.4. Preparation of polycarbosilane from trichloromethylsilane and diethoxymethylvinylsilane (PCS 3)

Polycarbosilane was prepared by the sodium metal mediated copolymerization of diethoxymethylvinylsilane with trichloromethylsilane in a proportion of 1:1. The monomer to sodium metal ratio was maintained as 1:1. The reactions were done in toluene, as solvent under nitrogen atmosphere.



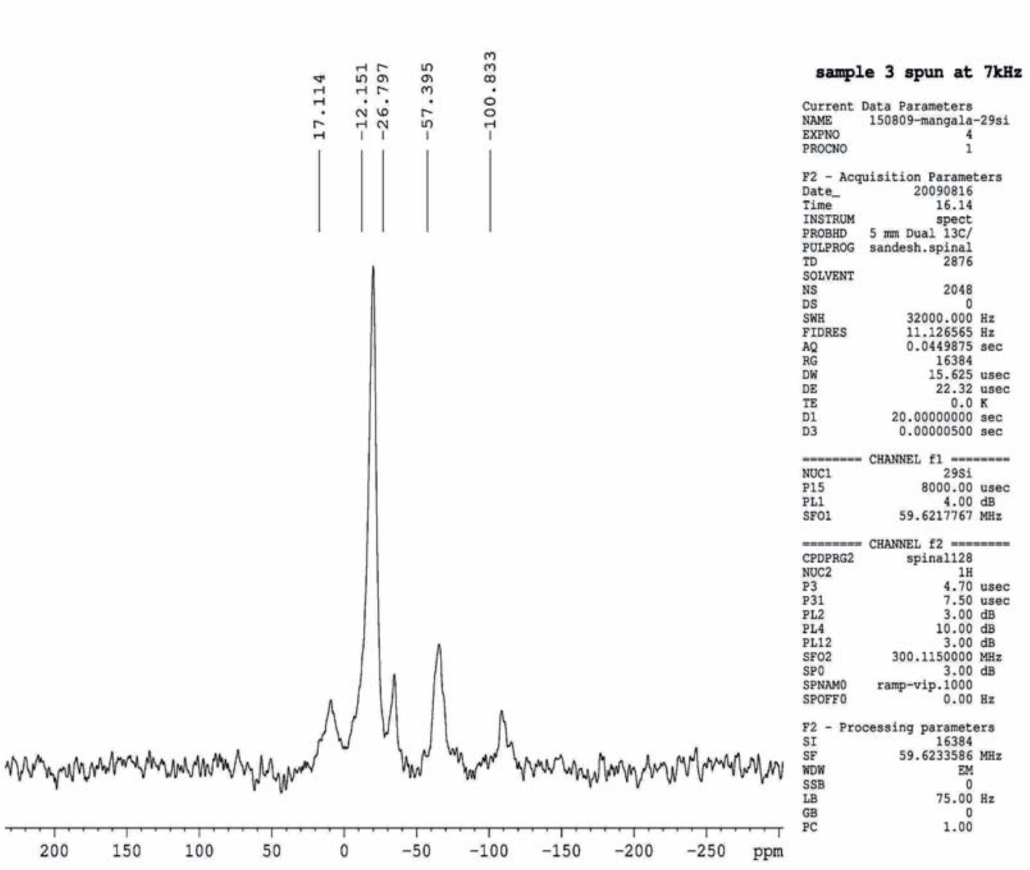
Scheme 4: Preparation of PCS 3

The product was obtained as two fractions, one as a viscous liquid with brown colour which was soluble in toluene and a white solid which was insoluble in all solvents. The molecular weight was determined for liquid fraction by GPC technique using polystyrene as standard and toluene as solvent. The liquid oligomer had a molecular weight Mn = 650, Mw =854 from GPC.

The insoluble polycarbosilane was analysed with TG-DTA, XRD analysis, FT-IR spectroscopy, ^{13}C NMR spectroscopy and ^{29}Si NMR spectroscopy.

Infrared spectrum of PCS 3 exhibited peaks at 2967 cm^{-1} corresponding to C-H stretching in Si-CH_3, 1642 and 1414 cm^{-1} due to C-H stretching or CH_2 deformation in Si-CH_3, 1258 cm^{-1} to Si-CH_3 deformation, 1076 cm^{-1} to CH_2 wagging in Si-CH_2-Si, 777 cm^{-1} due to Si-CH_3 wagging and Si-C stretching.

The peaks assigned to Si-O-Si bonds are observed, peak around 1030 cm^{-1} was observed as superimposed on 1076 cm^{-1} which was due to the Si-O stretching of Si-OH bond. This peak intensified with prolonged air exposure, polymer might have oxidised during the handling and recording processes.



sample 3 spun at 7kHz

```
Current Data Parameters
NAME       150809-mangala-29si
EXPNO                        4
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20090816
Time                     16.14
INSTRUM                  spect
PROBHD        5 mm Dual 13C/
PULPROG     sandesh.spinal
TD                        2876
SOLVENT
NS                        2048
DS                           0
SWH              32000.000 Hz
FIDRES           11.126565 Hz
AQ               0.0449875 sec
RG                       16384
DW                  15.625 usec
DE                   22.32 usec
TE                     0.0 K
D1             20.00000000 sec
D3              0.00000500 sec

======== CHANNEL f1 ========
NUC1                      29Si
P15                8000.00 usec
PL1                   4.00 dB
SFO1           59.6217767 MHz

======== CHANNEL f2 ========
CPDPRG2             spinal128
NUC2                        1H
P3                    4.70 usec
P31                   7.50 usec
PL2                   3.00 dB
PL4                  10.00 dB
PL12                  3.00 dB
SFO2          300.1150000 MHz
SPO                   3.00 dB
SPNAM0         ramp-vip.1000
SPOFF0                0.00 Hz

F2 - Processing parameters
SI                       16384
SF              59.6233586 MHz
WDW                         EM
SSB                          0
LB                       75.00 Hz
GB                           0
PC                        1.00
```

Figure 8: ^{29}Si CP-MAS NMR spectrum of PCS 3

^{29}Si CP-MAS NMR spectrum of PCS3 is shown in Figure 8. Chemical shifts are based on tetramethylsilane as internal standard. In the spectrum, the peak around 17.11 ppm was assigned to be due to the resonance of *Si*-O-Si unit, which would have resulted by the oxidation of the polymer, peak at -12.15 ppm was due to the resonance of Si in the $(CH_3)\mathit{Si}(CH_2)_2$ linkage, peak around -26.79 ppm corresponded to $(CH_2)_2\mathit{Si}$ Si unit, peak around -57.39 ppm corresponded to the *Si*-*Si* linkage which was formed by the consequence of head to head polymerization.

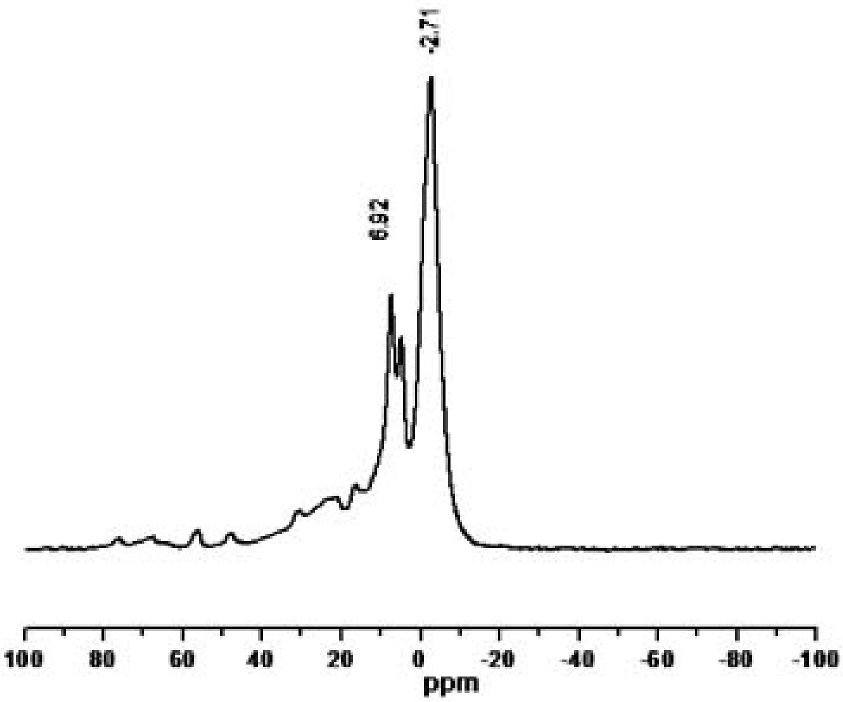
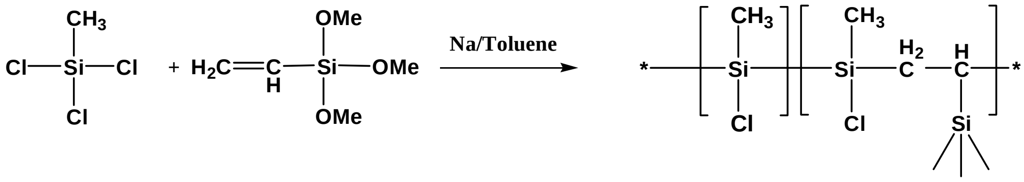


Figure 9: ^{13}C NMR spectrum of PCS 3

Figure 9 presents the solid state ^{13}C-NMR spectrum of PCS 3. It exhibits two major broad peaks around 6.92 ppm and -2.71 ppm, which are mainly assigned to the signal of SiSiCH_3 units and Si-CH_2 respectively. The absence of signal around 60 ppm indicates the absence of unreacted alkoxy group in the prepared polymer.

2.2.5. Preparation of polycarbosilane from trichloromethylsilane and trimethoxyvinylsilane (PCS 4)

Polycarbosilane was prepared by the sodium metal mediated copolymerization of trimethoxyvinylsilane with trichloromethylsilane in a ratio of 1:1. The monomer to sodium metal ratio was retained as 1:1. The reactions were done in toluene, as solvent and under nitrogen atmosphere.



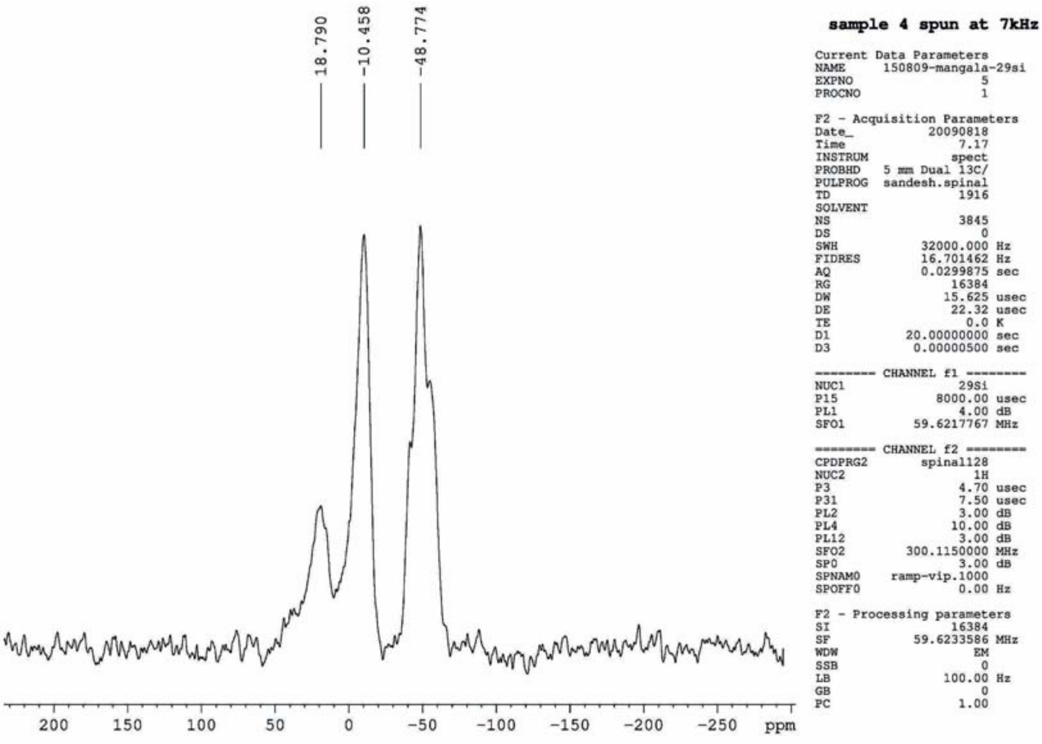
Scheme 5: Preparation of PCS 4

The product was obtained as two fractions, one as a viscous liquid which was soluble in toluene and a white solid which was insoluble in all solvents. The molecular weight was determined for the liquid fraction by GPC technique using polystyrene as standard and toluene as solvent. The liquid oligomer have a molecular weight Mn = 596, Mw =992 from GPC. The liquid fraction was discarded.

The insoluble polycarbosilane was analysed with TG-DTA, XRD pattern, FT-IR spectroscopy, ^{13}C NMR spectroscopy and ^{29}Si NMR spectroscopy.

The FT-IR spectrum of the polymer has the corresponding peaks of the polycarbosilane. Peak at 1453, 1270, 1082, 783 cm^{-1} are clearly seen in the spectrum which corresponded to the $CHSiCH_3$ and SiC. The spectrum showed a peak at 2929cm^{-1} which was corresponding to the C-H stretching, 1635, 1453 cm^{-1} due to $Si-CH_3$ stretching, 1270 cm^{-1} corresponding to $Si-CH_3$ deformation,1082 cm^{-1} due to CH_2 wagging in $Si-CH_2-Si$ bond and 783 cm^{-1} due to $Si-CH_3$ wagging.

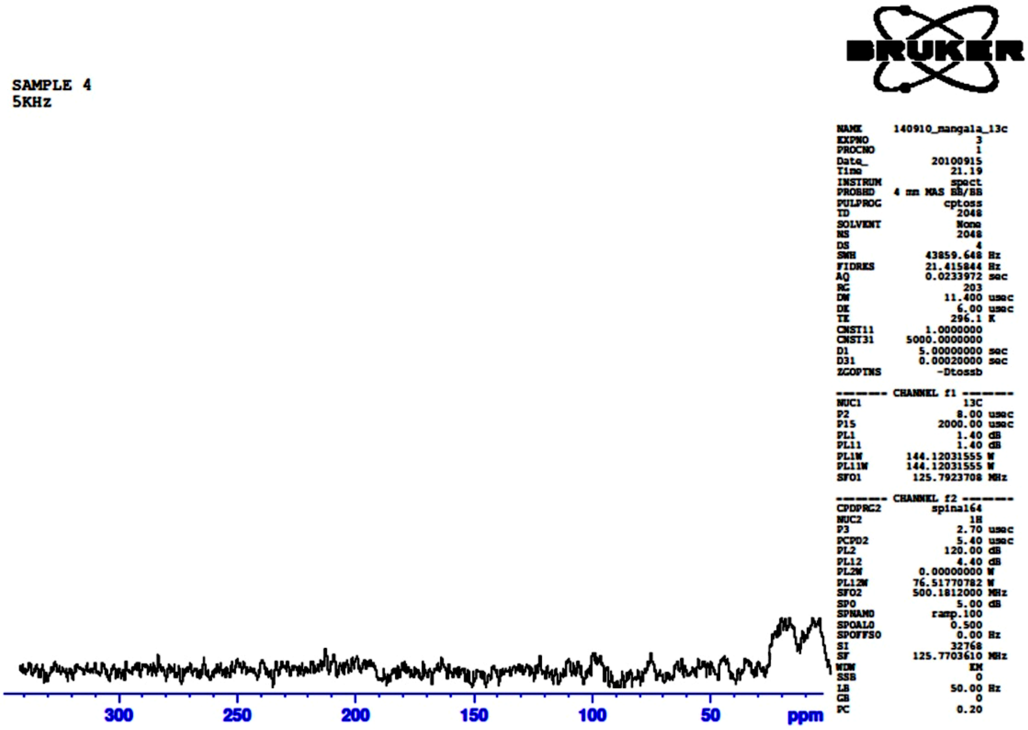
1032 cm^{-1} seen as superimposed on 1082 cm^{-1} was due to the Si-O stretching of Si-OH bond. The peaks assigned to Si-O-Si bonds (around 1032 cm^{-1}) are observed, which intensified with prolonged air exposure, polymers might have oxidised during the handling and measuring processes.



```
sample 4 spun at 7kHz

Current Data Parameters
NAME     150809-mangala-29si
EXPNO                      5
PROCNO                     1

F2 - Acquisition Parameters
Date_               20090818
Time                    7.17
INSTRUM                spect
PROBHD    5 mm Dual 13C/
PULPROG   sandesh.spinal
TD                      1916
SOLVENT
NS                      3845
DS                         0
SWH             32000.000 Hz
FIDRES          16.701462 Hz
AQ             0.0299875 sec
RG                     16384
DW             15.625 usec
DE              22.32 usec
TE                   0.0 K
D1          20.00000000 sec
D3           0.00000500 sec

======== CHANNEL f1 ========
NUC1                    29Si
P15            8000.00 usec
PL1                 4.00 dB
SFO1         59.6217767 MHz

======== CHANNEL f2 ========
CPDPRG2            spinal128
NUC2                      1H
P3                4.70 usec
P31               7.50 usec
PL2                 3.00 dB
PL4                10.00 dB
PL12                3.00 dB
SFO2        300.1150000 MHz
SP0                 3.00 dB
SPNAM0      ramp-vip.1000
SPOFF0              0.00 Hz

F2 - Processing parameters
SI                     16384
SF           59.6233586 MHz
WDW                       EM
SSB                        0
LB                100.00 Hz
GB                         0
PC                      1.00
```

Figure 10: ^{29}Si CP-MAS NMR spectrum of PCS 4

^{29}Si CP-MAS NMR spectrum of the PCS 4 is presented in figure 10. Spectrum gives a clear idea about the structure of the polycarbosilane. Peaks are mainly distributed in two regions. Peak around -10.45ppm corresponds to $CH_3\mathit{Si}(CH_2)_2$ linkage and -48.77 ppm peak is of *Si*-Si linkage; formed by the head to head polymerization of the monomers. A small peak at 18.79ppm corresponds to *Si*-O-Si linkage which might be formed by the oxidation of the polymer.



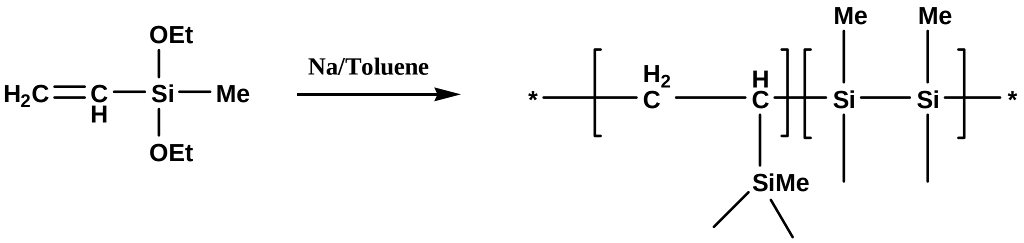
```
NAME        140910_mangala_13c
EXPNO                        3
PROCNO                       1
Date_                 20100915
Time                     21.19
INSTRUM                  spect
PROBHD      4 mm MAS BB/BB
PULPROG                 cptoss
TD                        2048
SOLVENT                   None
NS                        2048
DS                           4
SWH                  43859.648 Hz
FIDRES               21.415844 Hz
AQ                   0.0233972 sec
RG                         203
DW                      11.400 usec
DE                        6.00 usec
TE                       296.1 K
CNST11               1.0000000
CNST31            5000.0000000
D1                  5.00000000 sec
D31                 0.00020000 sec
ZGOPTNS                -Dtossb

======= CHANNEL f1 =======
NUC1                       13C
P2                        8.00 usec
P15                    2000.00 usec
PL1                       1.40 dB
PL11                      1.40 dB
PL1W              144.12031555 W
PL11W             144.12031555 W
SFO1               125.7923708 MHz

======= CHANNEL f2 =======
CPDPRG2              spinal64
NUC2                        1H
P3                        2.70 usec
PCPD2                     5.40 usec
PL2                     120.00 dB
PL12                      4.40 dB
PL2W                0.00000000 W
PL12W              76.51770782 W
SFO2               500.1812000 MHz
SP0                       5.00 dB
SPNAM0                ramp.100
SPOAL0                   0.500
SPOFFS0                   0.00 Hz
SI                       32768
SF                 125.7703610 MHz
WDW                         EM
SSB                          0
LB                       50.00 Hz
GB                           0
PC                        0.20
```

Figure 11: ^{13}C NMR spectrum of PCS 4

Figure 11 presents the solid state ^{13}C-NMR spectrum of PCS 4. It exhibits two major broad peaks around 6 and 20 ppm, which are mainly assigned to the signal of $SiSiCH_3$ units and CH_2-CH_2 respectively. The absence of signal around 60 ppm indicates the absence of unreacted alkoxy group in the prepared polymer.

2.2.6. Preparation of polycarbosilane from Diethoxymethylvinylsilane (PCS 5)

Polycarbosilane was prepared by the sodium metal mediated homopolymerization of diethoxymethylvinylsilane. The monomer to sodium metal ratio was maintained as 1:1. The reaction was done in toluene, as solvent and under nitrogen atmosphere.



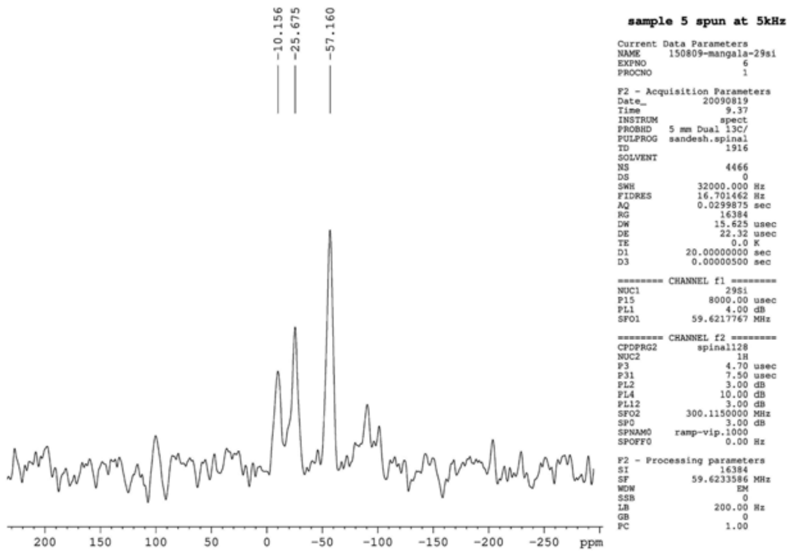
Scheme 6: Preparation of PCS 5

The product was obtained as two fractions, one as a viscous liquid which was soluble in toluene and a white solid which was insoluble in all solvents. The molecular weight was determined for liquid fraction by GPC technique using polystyrene as standard and toluene as solvent. The liquid oligomer had a molecular weight Mn = 690, Mw =872 as obtained from GPC.

The insoluble solid polymer was used for further studies. It was analysed with TG-DTA, XRD analysis, FT-IR, ^{13}C NMR and ^{29}Si NMR spectroscopy.

Infrared spectrum of PCS 5 has the peaks at 2961 cm^{-1} corresponding to C-H stretching in Si-CH_3, 1647 and 1407 cm^{-1} due to C-H stretching or CH_2 deformation in Si-CH_3, 1264 cm^{-1} due to Si-CH_3 deformation, 1095 cm^{-1} due to CH_2 wagging in Si-CH_2-Si, 790 cm^{-1} due to Si-CH_3 wagging and Si-C stretching.

The peak at 1031 cm^{-1} was seen as superimposed on 1095 cm^{-1} which was the peak assigned to Si-O-Si bond (around 1031 cm^{-1}) observed in the polymer, since this peak intensified with continuous air exposure; polymers might have oxidised during the handling and recording processes.



```
sample 5 spun at 5kHz

Current Data Parameters
NAME      150809-mangala-29si
EXPNO                   6
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090819
Time                 9.37
INSTRUM             spect
PROBHD    5 mm Dual 13C/
PULPROG   sandesh.spinal
TD                   1916
SOLVENT
NS                   4466
DS                      0
SWH            32000.000 Hz
FIDRES         16.701462 Hz
AQ             0.0299875 sec
RG                  16384
DW                 15.625 usec
DE                  22.32 usec
TE                    0.0 K
D1            20.00000000 sec
D3             0.00000500 sec

======== CHANNEL f1 ========
NUC1                 29Si
P15               8000.00 usec
PL1                  4.00 dB
SFO1           59.6217767 MHz

======== CHANNEL f2 ========
CPDPRG2         spinal128
NUC2                   1H
P3                   4.70 usec
P31                  7.50 usec
PL2                  3.00 dB
PL4                 10.00 dB
PL12                 3.00 dB
SFO2          300.1150000 MHz
SP0                  3.00 dB
SPNAM0     ramp-vip.1000
SPOFF0               0.00 Hz

F2 - Processing parameters
SI                  16384
SF             59.6233586 MHz
WDW                    EM
SSB                     0
LB                 200.00 Hz
GB                      0
PC                   1.00
```

Figure 12: ^{29}Si CP-MAS NMR spectrum of PCS 5

^{29}Si CP-MAS NMR spectrum of the PCS 5 is shown in figure 12. Peak around -10.15 ppm corresponds to $CH_3\mathit{Si}(CH_2)_2$ linkage and -25.67 ppm peak is due to the $CH_2\mathit{Si}CH_2$ group, a peak around -57.16 ppm which is an evidence for *Si*-Si linkage; formed by the head to head polymerization of the monomers.

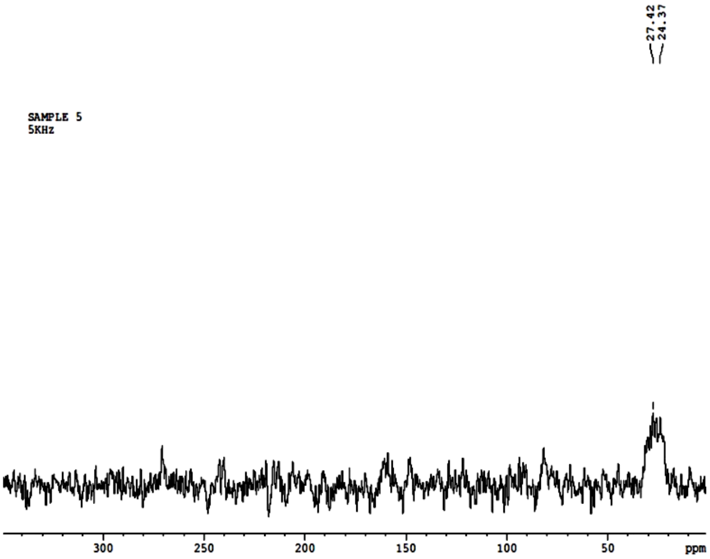


Figure 13: ^{13}C NMR spectra of PCS 5

The solid state ^{13}C NMR spectrum of PCS 5 (shown in figure 13) exhibits only one resonance signal centered at 20 ppm, which is a broad signal ranging from 10 ppm to 30 ppm. This is mainly assigned to the signal of CH_2-CH_2 unit. There is no signal around 120 ppm and 60 ppm, which indicate the absence of unreacted vinyl groups and alkoxy groups in the prepared polymer.

2.2.7. Halide Estimation

The quantitative chlorine estimation of the polycarbosilanes was done by modified Volhard's method[27]. The chlorine estimation was done for all the synthesized polycarbosilanes except PCS 5. All other polycarbosilanes gave expected results for the estimation and the results are listed in table 1.

Table 1: Chlorine estimation of polycarbosilanes

Polymer	PCS 1	PCS 2	PCS 3	PCS 4
Chlorine (mmol/g)	3.9	5.1	4.5	4.1

2.2.8. Thermal properties of polycarbosilanes

Inorder to investigate the thermal behaviour of the polycarbosilanes; the TG-DTA analysis was done. The polycarbosilanes were subjected to temperature scan from 50 to 1000°C in N_2 atmosphere at a rate of 20°C/min. The result is illustrated in figure 14.

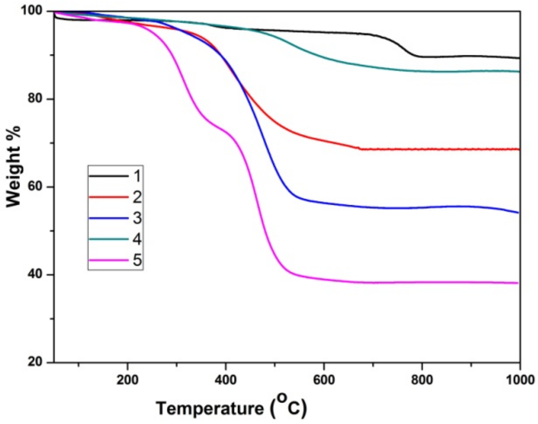


Figure 14: Thermogravimetric analysis of polycarbosilanes

In the TGA curve, 3% weight loss below 300°C is attributed to the vaporization of low molecular weight oligomers. From 300-800°C the weight loss is due to the release of gaseous products such as methane and hydrogen during the conversion of the Si-Si bond to Si-C bond. No obvious weight loss was observed in the range of 800-1000°C. High temperature stability is attributed to substantial cross-linking in PCS.

The TGA residues of the polycarbosilanes are given in table 2.

Table 2: TGA residue of the polymers

Entry	**TGA residue at 1000°C (%)**
PCS 1	89
PCS 2	68
PCS 3	54
PCS 4	86
PCS 5	38

From the TGA curves it is clear that out of the five polycarbosilanes, PCS 1 and PCS 4 have highly cross-linked structure. PCS 1, polycarbosilane prepared by the thermolysis of polysilane gave high char yield. It has low volatile substituents because it had under gone thermolysis prior to analysis. During thermolysis the low volatile fractions might have undergone evaporation and hence high char yield. Polycarbosilane prepared by the homopolymerization of diethoxymethylvinylsilane (PCS 5) have low char yield. This may be because of the less cross-linked nature of the polymer. Other polymers PCS2 and PCS3 gave average char yield.

2.2.9. X-Ray diffraction analysis

X-ray diffraction analysis of all the polycarbosilanes was performed. The sample was scanned over the range of 20°-90° angles with an increment of 0.05 ° angle and with the rotation speed of 5°/min.

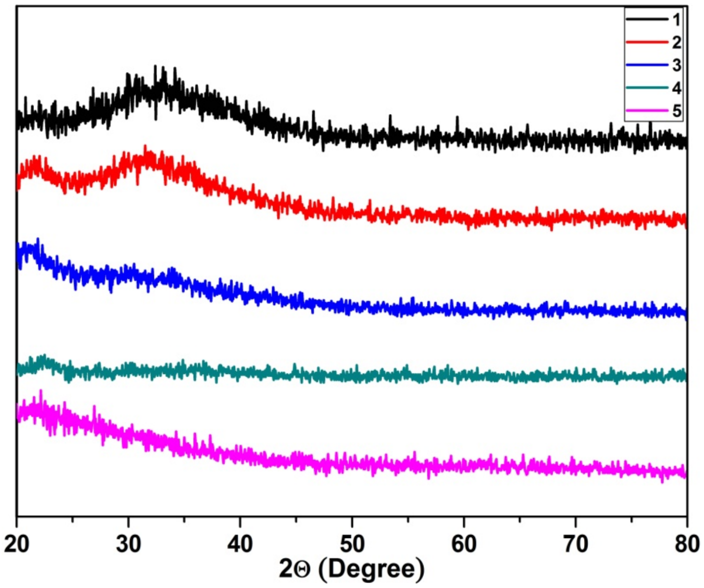


Figure 15: X-Ray Diffraction pattern of the polycarbosilanes

The XRD pattern of the polycarbosilanes clearly reveals their amorphous nature; which can be explained due to the cross-linked structure of the polymers.

2.2.10. Surface Area Analysis

Nitrogen gas adsorption methods are commonly employed to determine surface area and pore size distribution of solids. The polycarbosilanes are subjected to surface area analysis by BET surface area analyzer. Results are tabulated (table 3).

Table 3: Results of BET surface area analysis

Sample	Surface area (m^2/g)	
	BET	**Langmuir**
PCS 1	333.3	506.2
PCS 2	229.4	458.5
PCS 3	203.6	397.8
PCS 4	679.3	1171.2
PCS 5	154.2	275.2

The high surface area of PCS 4 is attributed to its high cross-linked structure. And PCS 4 has mesoporous nature also. The thermogravimetric analysis results are in good agreement with these results. From the surface area results it is clear that the homopolymer prepared from diethoxymethylvinylsilane has low surface area which can be explained because of its less cross-linked nature.

2.3. Conclusion

Preparation of five polycarbosilanes was done successfully. Halogen estimation was done by Volhard's method. The polycarbosilanes were characterised using various analytical techniques such as UV-Vis DRS, TG-DTA, X-ray diffraction analysis, FT-IR spectroscopy, ^{13}C NMR spectroscopy, ^{29}Si NMR spectroscopy and surface area analysis. From the results of analytical data the structure of polycarbosilanes was deducted. All the polycarbosilanes are of highly cross-linked structure and amorphous in nature. All of them possess high temperature stability and high surface area. The polycarbosilanes, except PCS 5, are capable of further functionalization. The functionalization of polycarbosilanes can be used to make use of the polycarbosilanes in a variety of applications.

2.4. Experimental

2.4.1. Preaparation of polycarbosilane

2.4.1.1. Preparation of polycarbosilane 1 (PCS 1)

2.4.1.1.1. Preparation of polymethyl silane

Trichloromethylsilane was used as the monomer. Sodium metal (1.2g, 54.375mmol) in anhydrous toluene (50mL) was refluxed and stirred vigorously to make a dispersion. Trichloromethylsilane (6.4mL, 54.375mmol) was added drop wise. The reaction was highly exothermic. After the addition of monomers, the reaction mixture was refluxed for 12h. It was cooled and the suspension obtained was filtered, washed with methanol and dried. The whole process was carried out under Nitrogen atmosphere. Yield: 47%.

2.4.1.1.2. Thermolysis of polymethylsilane to polycarbosilane

The polysilane obtained by the Wurtz coupling of trichloromethylsilane was taken in a silica crucible and was heated upto 400^{o}C in a muffle furnace for 4h. A colourless powder was obtained. The polysilane has undergone Kumada rearrangement and gave cross-linked polycarbosilane.

2.4.1.2. Preparation of PCS 2

In a 250mL round bottom flask, the Sodium metal (2.5g, 108.75mmol) in anhydrous toluene (50mL) was refluxed and stirred vigorously to make dispersion. A mixture of trichloromethylsilane (6.4mL, 54.375mmol) and chlorodimethylvinylsilane (7.4mL, 54.375mmol) was added drop wise. The reaction was highly exothermic. After the addition of monomers, the reaction mixture was refluxed for 12h. It was cooled and the obtained suspension was filtered, washed with methanol and dried. The whole process was carried out under Nitrogen atmosphere. Yield: 48 %.

2.4.1.3. Preparation of PCS 3

In a 250mL round bottom flask, the Sodium metal (2.5g, 108.75mmol) in anhydrous toluene (50mL) was refluxed and stirred vigorously to make dispersion. A mixture of trichloromethylsilane (6.4mL, 54.375mmol) and diethoxymethylvinylsilane (10.24 mL, 54.375mmol) was added drop wise. The reaction was highly exothermic. After the addition of monomers, the reaction mixture was refluxed for 12h. It was cooled and the obtained suspension was filtered, washed with methanol and dried. The whole process was carried out under Nitrogen atmosphere. Yield: 14g (47%).

2.4.1.4. Preparation of PCS 4

In a 250mL round bottom flask, the Sodium metal (2.5g, 108.75mmol) in anhydrous toluene (50mL) was refluxed and stirred vigorously to make dispersion. A mixture of trichloromethylsilane (6.4mL, 54.375mmol) and trimethoxyvinylsilane (8.13mL, 54.375mmol) was added drop wise. The reaction was highly exothermic. After the addition of monomers, the reaction mixture was refluxed for 12h. It was cooled and the obtained suspension was filtered, washed with methanol and dried. The whole process was carried out under Nitrogen atmosphere. Yield: 50 %.

2.4.1.5. Preparation of PCS 5

In a 250mL round bottom flask, the Sodium metal (1.2g, 54.375mmol) in anhydrous toluene (50mL) was refluxed and stirred vigorously to make dispersion. Diethoxymethylvinylsilane (10.24 mL, 54.375mmol) was added drop wise. The reaction was highly exothermic. After the addition of monomer, the reaction mixture was refluxed for 12h. It was cooled and the obtained suspension was filtered, washed with methanol and dried. The whole process was carried out under Nitrogen atmosphere. Yield: 60 %.

2.4.4. Estimation of chlorine capacity of the polymers

Chlorine analysis was done by the modified Volhard's method. The polycarbosilane (250mg) was heated with pyridine (2.5mL) for 1 h at 100°C, and the suspension was diluted with acetic acid: water (1:1) (25mL). The halide was displaced by the addition of Con.HNO_3 (5mL) and precipitated with a measured excess of standard $AgNO_3$ solution. AgCl that was formed was coated with toluene, and the excess $AgNO_3$ was back titrated with standard NH_4SCN solution, using ferric alum [$FeNH_4(SO_4).12H_2O$] as indicator. A red colour due to the formation of $Fe(SCN)_3$, indicates that an excess of SCN^- is present and that the end-point has been reached.

2.5. References

1. Seyferth, D. *Inorganic and Organometallic Polymers, ACS Symposium Series*, **1988,** *360*, 21.
2. Yajima, S.; Hayashi, J.; Omori, M. US Patent, 4,052,430, **1977.**
3. Czubarow, P.; Seyferth, D. *J. Mater. Sci.*, **1997,** *32*, 2121.
4. Cao, F.; Kim, D.; Li, X.; *J. Mater. Chem.* **2002**, *12*, 1213.
5. Huang, M.; Fang, Y.; Li, R.; Huang, T.; Yu, Z.; Xia, H. *J. Applied Polymer Science,* **2008,** *113*, 1611.
6. Interrante, L.V.; Rushkin, I.; Shen, Q. *Appl. Organometal. Chem.* **1998**, *12*, 695.
7. Birot, M.; Pillot, J.P.; Dunogues, J. *Chem. Rev.* **1995,** *95*, 1443.
8. Zeigler, J.M.; Fearon, F.W.G. *'Silicon-Based Polymer Science A Comprehensive Resource, Advances in Chemistry Series 224"*, **1990**, Washington, DC, American Chemical Society.
9. Schilling, C.L.; Hudson, C.O.; William, T.C.; Wesson, J.P. US Patent, 4,497,787, **1985.**

10. Iseki, T.; Narisawa, M.; Katase, Y.; Oka, K.; Dohmaru, T.; Okamura, K. *Chem. Mater.* **2001**, *13*, 4163.
11. Greenberg, S.; Clendenning, S. B.; Liu, K.; Manners, I. *Macromolecules*, **2005**, *38*, 2023.
12. Kawakami, Y.; Nakao, K.; Shinke, S.; Imae, I. *Macromolecules*, **1999**, *32*, 6874.
13. Narula, C. K.; Allison, J. E.; Bauer, D. R.; Gandhi, H. S. *Chem. Mater.*, **1996**, *8*, 984
14. Tsirlin, A.M.; Shcherbakova, G.I.; Florina, E.K.; Popova, N.A.; Gubin, S.P.; Moroz, E.M.; Riedel, R.; Kroke, E.; Steen, M. *J. European Ceramic Society*, **2002**, *22*, 2577.
15. Krawiec, P.; Kockrick, E.; Borchardt, L.; Geiger, D.; Corma, A.; Kaskel, S. *J. Phys. Chem, C.,* **2009**, *113*, 7755.
16. Oyamada, H.; Akiyama, R.; Hagio, H.; Naito, T.; Kobayashi, S. *Chem. Commun.* **2006**, *31*, 5609.
17. Ganicz, T.; Stanczyk, W.A.; Chmielecka, J.; Kowalski, J. *Polym. Int.,* **2008**, *58*, 248.
18. Sakurai, Y.; Yoshimura, D.; Ishii, H.; Ouchi, Y.; Isaka, H.; Teramae, H.; Matsumoto, N.; Hasegawa, S.; Ueno, N.; Seki.; K. *J. Phys. Chem. B* **2001**, *105,* 5626.
19. Ganicz, T.; Stanczyk, W.A. *Macromolecules*, **2000**, *33*, 289.
20. Wang, X.; Yuan, Y.; Graiver, D.; Cabasso, I. *Macromolecules*, **2007**, *40,* 3939.
21. Lee, Y.J.; Lee, J.H.; Kim, S.R.; Kwon, W.T.; Klepeis, J.P.; Teat, S.J.; Kim, Y.H. *J. Mater. Sci.*, **2010**, *45*, 1025.
22. Schilling, C.L.; Hudson, C.O.; William, T.C. US Patent, 4,472,591, **1984**.

23. Chen, J.; He, G.; Liao, Z.; Zeng, B.; Ye, J.; Chen, L.; Xia, H.; Zhang, L. *J. Appl. Polymer Sci.*, **2008**, *108*, 3114.
24. Rushkin, I. L.; Shen, Q.; Lehman, S. E.; Interrante, L. V. *Macromolecules*, **1997**, *30*, 3141.
25. Dvornic, P. R.; Owen, M. J.; *Silicon-Containing Dendritic Polymers*, **2009**, Canada, Springer.
26. Komuro, K.; Kawakami, Y. *Polymer Bulletin*, **1999**, *42*, 669.
27. Yan, B.; Czarnik, A. W. '*Optimization of Solid- Phase Combinatorial Synthesis'* **2002**, New York, Marcel Dekker.
28. Miller, R. D.; Michl, J.; *Chem. Rev.* **1989**, *89*, 1359.

Chapter 3

INCORPORATION OF METAL IONS ON POLYCARBOSILANES: SYNTHESIS AND CHARACTERIZATION

Contents

3.1. Introduction

Polycarbosilanes have found applications as lithographic resists, liquid crystals and are of considerable technological importance due to their electrical and magnetic properties apart from their use as ceramic precursors.[1-2] It is clear that various substituents play a crucial role on the polymer properties. Nucleophilic substitution reaction has been used extensively to add side chains or to modify the structure of the initially obtained polycarbosilane through reaction with Si-Cl or Si-OR groups on the polymer backbone.[3-5] This methodology has been, and is likely to continue to be, an important component of the chemical tool kit that is available for the preparation and effective utilization of this important class of organosilicon polymers.

However, hyperbranched polycarbosilane with specific functional groups have applications other than their use as preceramic polymers. For example, hyperbranched polycarbosilane bearing pendant oligoethyleneoxo groups dissolves various LiX salts and exhibit appreciable Li^+ ion conductivity. Their potential use as electrolytes in Li batteries has been suggested.[6] Also, a thin film made by sol-gel processing of an alkoxy-substituted hyperbranched polycarbosilane has excellent mechanical properties.[7] This film has been patented for the use as an interlayer dielectric (ILD) in semiconductor processing and is now commercially available. A chemical sensor for the detection of explosives made from hyperbranched polycarbosilanes with hydroxyl substituted groups has also been claimed.[8]

Liquid crystal side chain polymers, based on a polycarbosilane backbone, have become a new area of interest in recent years. The important features of this novel class of liquid crystal materials allow for creation of a wide spectrum of thermotropic properties with in the same type of main polymer chain, by varying the number of carbon and silicon atoms in the side chain. Polycarbosilanes exhibit intermediate phase transition temperatures, covering a useful range of mesophase generation. Depending on the type of mesogens, the liquid crystal phase exists typically between 25 and 110°C, which is attractive from the point of view of applied studies.[9-11] It is significant that incorporation of silicon atoms into a carbon polymer skeleton increase the flexibility of the system as a result of a considerable difference in carbon and silicon atomic radius; 77 and 117 pm.

Additionally, the advantage of the liquid crystal polycarbosilanes, compared to the recommended polysiloxanes, is that they exhibit higher thermal stability and are resistant to the redistribution process of monomeric units, under basic conditions. Liquid crystal polycarbosilanes are extensively studied as stationary phases in gas-liquid chromatography. They have unique separation properties when used in gas chromatography.[11]

Metal incorporated polycarbosilanes[12-14] are attractive lithographic resists for the formation of patterned, functional, metal containing ceramics due to their excellent film forming ability and high concentration of metal exhibiting ferromagnetism.[10,15] These offer access to ordered arrays of magnetic ceramics containing metal nanoparticles. The nanostructures may find applications in spintronics as an isolating magnetic layer in a nanogranular in-gap structure.

The wish to combine the advantages and exclude the short comings of homogeneous and heterogeneous catalysis has led to the creation of 'hybrid-phase' catalytic systems. They feature a substantial restriction of the mobility of the (MXn) by chemically binding them to a polymeric or mineral support.[16-20] Implantation of metal complexes (homogeneous catalysts) into films, elastic granules, fibres, membranes and powders that can be easily isolated from the reaction mixture can be used many times in the same way as typical heterogeneous catalysts.

Recently, the area of polymer supported organic reactions and polymer-supported catalysts have been reviewed from the point of view of the solid phase synthetic chemistry which can be carried out on resins and the reactions that have been catalysed by polymer supported metal complexes.[21-29]

The synthesis of a polymer-metal complex represents an attempt to give inorganic functions to an organic polymer. Complexing and chelating sorbents find use in transition and alkaline earth metal ion separation and recovery of trace metal ions, catalysis, organic synthesis, water and waste water treatment, pollution control and as polymer drug grafts. Catalytically active polymers can be obtained by inducing a metal complex to catalyze a reaction with a polymer backbone and it is reasonable to assume that the metal complex bound to the polymer shows a specific type of catalytic behaviour reflecting the properties of the polymer chain. Indeed, many synthetic polymer metal complexes have been found to exhibit high catalytic efficiency. Thus research on catalytic activity of polymer-metal complexes has attracted considerable interest in recent years.[30,31]

3.2. Characterization of metal containing polycarbosilane

Various spectroscopic methods are useful in the characterization of metal incorporated polymers. The analytical techniques used are FT-IR, UV-Vis DRS, EPR spectroscopy and TG/DTA, magnetic susceptibility measurements, and AAS/ICP-AES for the estimation of metal content.

The structure of metal attached polymers are studied mainly by spectroscopic techniques such as FT-IR, UV-Vis DRS and ESR. Magnetic susceptibility measurements and thermogravimetric methods are widely used for the characterization of metal attached polymer. The latter technique is used commonly as a means of assessing the thermal stability of polymeric materials. FT-IR spectra can be used in locating the coordination sites of the metal salts. From ESR spectrum, the nature of metal coordination can ascertained. Electronic spectral data and magnetic moment values help in predicting the stereochemistry of the metal incorporated polymer.

3.2.1. Atomic Absorption Spectroscopy/ ICP-AES

The determination of metal ion content helps in the prediction of the co-ordination number and stereochemistry of the metal incorporated polymers. Atomic absorption spectroscopy (AAS) is a spectro-analytical technique for the qualitative and quantitative determination of elements. In analytical chemistry the technique is used for determining the concentration of a particular element in a sample. The technique makes use of Beer-Lambert law. It requires standards with known concentrations of the element to be analyzed to establish the relation between the measured absorbance and the sample concentration. By taking absorption spectrum of the standards and the sample, we can calculate the concentration of element to be analyzed in a sample. In short, the electrons of the atoms in the atomizer can be promoted to excited state by absorbing a defined quantity of energy. This amount of energy, i.e., wavelength, is specific to a particular electron transition in a particular element. In general, each wavelength corresponds to only one element, which gives the technique its elemental selectivity. The absorbance with standards and with a sample in the atomizer is measured using a detector, and the ratio between the values is converted to sample concentration or mass using Beer-Lambert Law.

3.2.2. Infrared spectroscopy

Infrared spectroscopy provides an excellent tool for characterising polymer metal complexes and to locate the co-ordination sites in them. The characteristic absorption due to a particular functional group often disappears completely on chemical transformation, with the simultaneous appearance of absorption bands corresponding to the new group. IR spectroscopy has mainly been used qualitatively to determine the extent to which a chemical transformation has taken place and also to show the presence of functional groups on polymer supports.

3.2.3. Nuclear Magnetic Resonance Spectroscopy

The application of NMR spectroscopy for the examination of polymers in the solid state by magic angle spinning (MAS) technique gives different structural information about the polymers. The MAS technique has become the most widely used method for obtaining high resolution spectra from solid materials. The introduction of the MAS (magic angle sample spinning; MASS) technique that allowed spectral resolution in solids sufficient to distinguish between chemical groups with different chemical shifts. In MASS, the sample is spun at several kilohertz around an axis that makes the so-called magic angle θ_m (which is ~54.74°, where $\cos^2\theta_m = 1/3$) with respect to the direction of the static magnetic field B_0; as a result of such magic angle sample spinning, the chemical shift anisotropy bands are averaged to their corresponding average (isotropic) chemical shift values. One notes that correct alignment of the sample rotation axis as close as possible to θ_m is essential for cancelling out the dipolar interactions.

A concept developed for transferring magnetization from protons to less sensitive nuclei is popularly known as cross-polarization. Cross-polarization under MAS conditions is also a powerful tool to detect low-abundant and low-sensitivity nuclei.

3.2.4. EPR spectroscopy

Application of EPR spectroscopy for monitoring the degree of functionalization of a polymer is limited primarily because EPR active groups are mostly used as probes rather than as reactive functionalities. EPR spectroscopy is being used in many cases to study the co-ordination structure of polymer complexes. The interaction between the spin of the central metal ion and the co-ordinated ligand decides the bonding pattern and its ‘g’ value which in turn is used to study the nature of the metal ligand bond.

Electron paramagnetic resonance measures the absorption spectra associated with the energy states produced from the ground state by interaction with the magnetic field. An electron in a magnetic field has two energies depending on its quantum numbers. The electron moments may be aligned parallel or antiparallel to the field giving rise to two energy states. The energy difference between the two m_s states is given by

$$\Delta E = h\nu = g\beta H,$$

Where h is Plank's constant, ν is the microwave frequency for transition from $m_s = +1/2$ to $m_s = -1/2$, g is the Lande splitting factor (equal to 2.0023 for a free electron), β is the Bohr magneton and H is the magnetic field.

'g' value depends on the orientation of a molecule with respect to the direction of an external magnetic field. In a transition metal complex, the electron is localised in a particular orbital and the coupling of the spin angular momentum and the orbital angular momentum gives rise to a 'g' value. Since the orbital degeneracy is partly removed in a metal complex, there is a net angular moment which gives rise to a different 'g' value from 2.0023. The spin-orbit contribution makes 'g' a characteristic property of a transition metal ion and its oxidation state.

Just as the electrons have spin, many nuclei are also known to possess spin. Nuclear spin quantum number (I) for each of the two m_s states of electron may be $m_I = +1/2$ and $m_I = -1/2$. The energy of a particular m_s state is affected by the nuclear spin-electron spin interaction energy. This energy varies as the product of m_s and m_I and is given by $Am_s.m_I$, where A is the hyperfine splitting constant. The constant A is characteristic of the degree of interaction of the unpaired electron with the nucleus. Interaction of the electron spin with nuclear spin gives 2I+1 number of EPR signals.

Usually the spectrum is recorded as a first derivative curve.

3.2.5. UV-Vis spectroscopy

Electronic spectra of metal complexes are generally used to study the geometry around the metal ions in the complex. The number and position of the bands give an idea of the geometry of the polymer complex. However the use is limited because of the low solubility of the polymer complexes in common solvents, their solution spectra cannot be obtained. Nevertheless the reflectance spectra of complexes are successfully used to find their geometries.

3.2.6. Magnetic susceptibility measurements

Measurements of the magnetic susceptibility form an integral part of the characterization of metal complexes. It gives an idea about the geometry of the metal bond in the complex. The magnetic moment value is a better tool in the hands of chemists for predicting the structure of the complexes of macromolecular ligands. In several studies, magnetic susceptibility measurements and Mossbauer parameters were used to establish the nature of various ion- exchange resins.

3.2.7. Thermogravimetric analysis

Thermogravimetric analysis is based on continuous recording of mass changes of a sample of material, as a function of a combination of temperature with time. This technique is used for assessing the thermal stability of polymeric materials. It also gives an idea about the changes of materials as the temperature increases. Samples were heated under nitrogen atmosphere from 50°C- 1000°C at a rate of 20°C/min.

3.2.8. Surface area analysis

Gas adsorption methods are most commonly employed to determine surface area and pore size distribution of solids. The amount of gas adsorbed by unit mass of adsorbate, V is related to the equilibrium pressure, P by means of the adsorption isotherm. Inspite of theoretical limitations, the Brunauer-Emmett-Teller method continues to be widely used for obtaining the adsorption isotherm data. The monolayer capacity Vm defined as the amount of adsorbate required to form a complete monolayer on the surface of unit mass of adsorbate, is obtained from BET equation.

$$\frac{P/P_0}{V(1-P/P_0)} = \frac{1}{V_mC} + \frac{C-1}{V_mC} \cdot \frac{P}{P_0}$$

P_0- saturation vapour pressure

C- const. related to the energy of the first layer of adsorption

The specific area As is

$$As = Vm \, . \, N_A \, . \, Am$$

N_A- avagadro's const.

Am- cross-sectional area of adsorbate molecule

N_2 is generally considered to be the most suitable adsorbate for the determination of surface area of solids. It is usually assumed that the BET nitrogen monolayer is close packed having

$$Am= 0.162 \text{ nm}^2$$

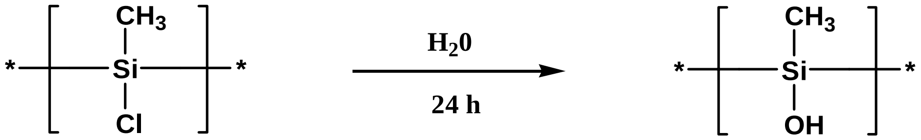
Prior to the measurement, the samples were degassed at room temperature for 12-16 h in N_2 flow.

The present chapter deals with the synthesis and characterization of metal containing polycarbosilanes. The polycarbosilanes formed by the polymerization of monomers such as trichloromethylsilane, chlorodimethylvinylsilane, diethoxymethylvinylsilane and trimethoxyvinylsilane, were used for the metal incorporation. The metal ions selected where Ti(IV), Mn(II), Co(II), Ni(II), Cu(II), Pd(II). The attachment of metal ions was done by the substitution reaction. The metal containing polycarbosilanes were characterized using various analytical methods. The spectroscopic techniques used are FT-IR, UV-Vis DRS, ^{29}Si-CP-MAS NMR, solid state- ^{13}C NMR, EPR spectroscopy. TG/DTA, magnetic susceptibility measurements, BET surface area analysis and AAS/ICP-AES were also used.

3.3. Results and Discussion

3.3.1. Preparation of hydroxyl substituted polycarbosilanes

The polycarbosilanes, except PCS 5, were treated with water to substitute chlorine atoms with hydroxyl groups. The substitution reaction was conducted in a round bottom flask; the polycarbosilanes were refluxed in water. It was then cooled and the suspension obtained was filtered and dried.



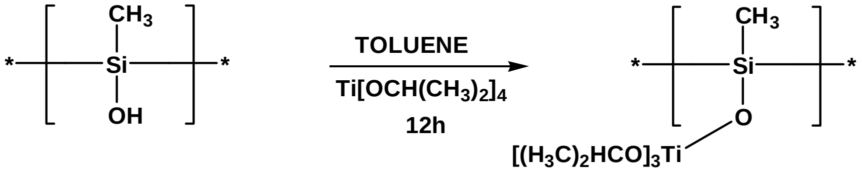
Scheme 1: Conversion of chlorine atoms of PCS to hydroxyl groups

The hydroxyl group substitution was confirmed by taking FT-IR spectrum of the product. The infra red spectrum showed a peak around 3448 cm^{-1}.

3.3.2. Incorporation of metal ions to polycarbosilanes

3.3.2.1. Incorporation of Titanium ions to polycarbosilanes

Polycarbosilane was stirred in toluene. Metal salt dissolved in ethanol (titanium isopropoxide and titanocene were added directly; not as an ethanol solution) to the swollen polymer. The titanium ion containing polycarbosilane was filtered, washed and dried. The metal containing polycarbosilane was characterized by UV-Vis DRS, FT-IR, ^{29}Si-CP-MAS NMR spectroscopy, TG-DTA, ICP-AES and surface area analysis. The metal ion concentration was estimated by ICP-AES.



Scheme 2: Titanium ion attachment to PCS

3.3.2.1.1. Factors influencing incorporation of titanium ion

PCS 2, which was obtained by the copolymerization of trichloromethylsilane and chlorodimethylvinylsilane, was selected as the polymer of choice to investigate the factors influencing incorporation of titanium ion. The factors like nature of metal salt, duration of the experiment, swelling agent and the reaction temperature were considered for the study.

3.3.2.1.1.1.Nature of the metal salt

Titanium was incorporated onto the polycarbosilanes using their corresponding salts. Inorder to study the extent of metal ion immobilization on polycarbosilanes, different types of salts for each metal were taken in to consideration.

Table 1: Effect of nature of the titanium compound on metal intake capacity

Metal compound	Metal content (m. equiv./g)
Titanium tetrachloride	1.67
Titanocence	2.20
Titanium isopropoxide	2.91

From the ICP-AES results, it is clear that the metal ion incorporation is high when titanium isopropoxide was used as the titanium source for incorporation. Thus it is selected as the source for titanium metal incorporation for further study.

3.3.2.1.1.2. Effect of swelling agent on the intake of titanium

The reaction using polycarbosilanes are heterogeneous in nature taking place in two distinct phases. Compatibility of the two phases is an important factor which controls the extent of complexation. Even though the polycarbosilane appears to be a solid insoluble in solvents; virtually it behaves as a gel which expands to a large extent in good solvents and the functional groups (OH) attached to the polymer are now exposed to the continuous phase. Strong interaction with the metal ions in solution and the solid polymers must occur for the reaction to take place.

The extent of complexation of polycarbosilane was studied in different solvents such as toluene, THF, xylene and ethanol. The polycarbosilane was suspended in different solvents and after swelling it was subjected to reaction with metal salt. Titanium isopropoxide was used directly for the reaction. The metal intake capacity was determined in each case and the results obtained are given in table 2.

Table 2: Influence of solvent on the metal intake capacity of PCS2*

Solvent	Metal content (m. equiv./g)
Toluene	2.91
THF	2.90
Xylene	2.91
Ethanol	1.91

*Temperature 323K, 12h

3.3.2.1.1.3.Metal intake capacity of PCS2 with time

To study the effect of reaction time on the metal incorporation of titanium on polycarbosilane, the metal content was estimated in a constant interval of time. The reaction was done at 50^{o}C. It is seen that, as the time increases from 6 h to 12 h a sharp increase in the metal content was obtained. But after 12 h no such sharp increase was observed. So we have selected the time for the experiment as 12 h.

Table 3: Effect of time on the metal intake capacity*

Time (h)	Metal content (m. equiv./g)
6	1.80
12	2.91
18	3.02
24	3.53

*Temperature 323K, swelling agent toluene

3.3.2.1.1.4. Effect of temperature on the incorporation of titanium ion

Temperature has a pronounced effect on the metal content. The macromolecular network with its functional groups produces additional segmental motion, due to increase in temperature. As a result of this additional segmental motion of the polymer, the metal ions are brought into closer contact with the reactive sites by penetration. Since the supporting macromolecular systems were thermally and mechanically stable, it could withstand changes in temperature. The influence of temperature on metal addition was studied at 303, 323 and 373 K. It was found that as the temperature was increased, the extent of binding of the polymer with metal salts also increased. The experiments were done by taking toluene as swelling agent and for 12 h.

Table 4: Metal intake capacity of PCS 2 at various temperatures*

Temperature (K)	Metal content (m. equiv./g)
303	1.80
323	2.91
373	4.43

*Time 12h, swelling agent toluene

3.3.2.1.2. Characterization of titanium attached polycarbosilane

3.3.2.1.2.1. Magnetic susceptibility measurements

From the magnetic susceptibility measurement results it is clear that the titanium incorporated polycarbosilanes are diamagnetic in nature. Thus it could be confirmed that the oxidation state of titanium bound to polycarbosilane is Ti (IV).

3.3.2.1.2.2. UV-Vis DRS analysis

Electronic spectra of titanium containing polycarbosilanes showed the peak around 490nm which corresponded to charge transfer transitions.

3.3.2.1.2.3. Infrared spectroscopy

In the reaction between PCS and titanium isopropoxide, it is presumed conventionally that –Ti(OR)$_3$ becomes a pendent group to PCS through the Si-O-Ti bond. When the Si-O-Ti bonds are formed, a strong absorption in the IR absorption spectrum is observed in the vicinity of 920 cm^{-1}. There is a chance for the hydrolysis of the bond between titanium and alkoxy group.

The FT-IR spectra of the Ti-PCS showed the peak corresponding to Si-O-Ti at 913 cm^{-1}.The spectra showed a broad band at 1024 cm^{-1} corresponding to Si-O vibration.

3.3.2.1.2.4. ^{29}Si-NMR spectroscopy

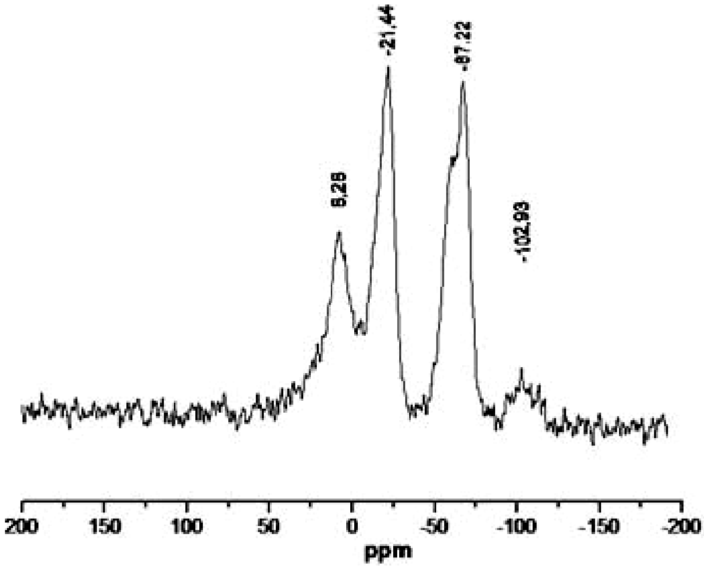


Figure 1: ^{29}Si CP-MAS NMR spectrum of Ti-PCS 4

^{29}Si CP-MAS NMR spectrum of the Ti-PCS 4 is shown in figure 1. Spectrum gives a clear idea about the metal attachment on polycarbosilane. New peaks in the region around -102.93 ppm correspond to the Ti-O-Si linkage. And it is seen that a total upfield shift of the polycarbosilane peaks has occured.

Peak around -10.45 ppm has been shifted to -22.15 ppm and -48.77 ppm to -68.34 ppm and small peak around 18.79 ppm was shifted to 7.77 ppm. This trend is explained due to the presence of titanium metal attached to the polycarbosilane.

3.3.2.1.2.5. ^{13}C CP-MAS NMR spectroscopy

^{13}C-NMR spectrum of titanium containing polycarbosilane 4 showed signals around 55.22 ppm, 30.45 ppm, 14.44 ppm and 4.14 ppm. The latter two peaks are due to the polycarbosilane and the former two ie, 55 ppm and 30 ppm corresponds to the peaks of isopropoxide moiety. From this we can confirm the metal attachment to the polycarbosilane.

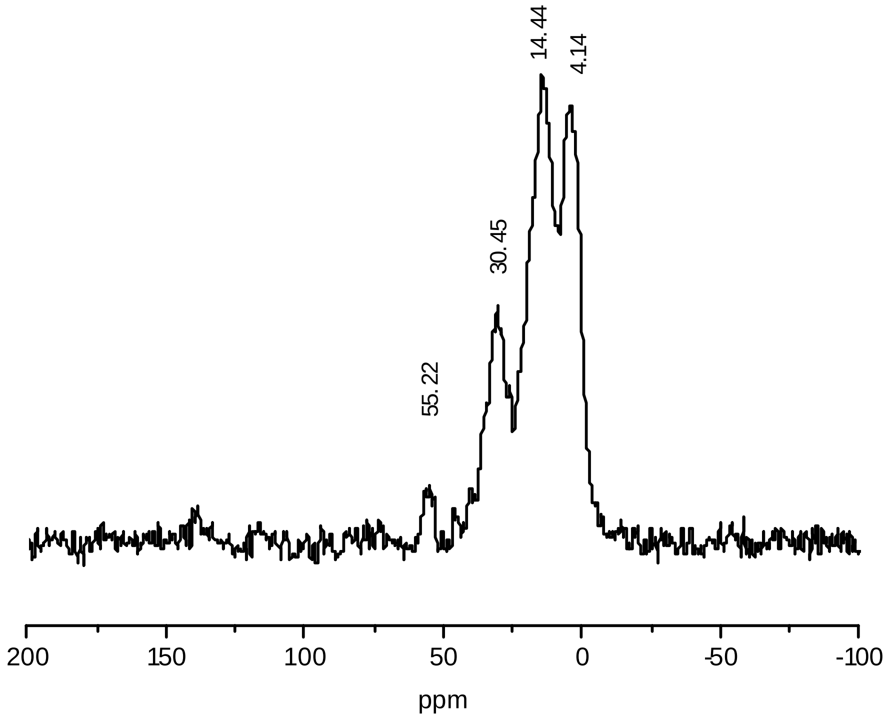


Figure 2: ^{13}C CP-MAS NMR spectrum of the Ti-PCS 4

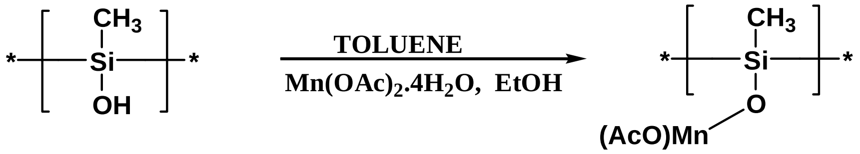
3.3.2.1.2.6. Thermogravimetric analysis

The thermogravimetric analysis of titanium containig polycarbosilane shows very small weight loss, which might be because of the evaporation of low molecular weight fractions of the polycarbosilane. It indicates the thermal stability of titanium incorporated polycarbosilane upto 1000°C.

3.3.2.2. Manganese containing Polycarbosilanes

Polymer was stirred in toluene to swell. Metal salt dissolved in ethanol was added to it and stirred. It was filtered and washed with methanol in a soxhlet extractor and dried. The manganese attached polycarbosilane was pale brown in colour.

The manganese containing polycarbosilane was characterized by UV-Vis DRS analysis, FT-IR, ^{13}C-NMR, ^{29}Si-CP-MAS NMR spectroscopy, magnetic susceptibility measurement, EPR analysis, TG-DTA, and surface area analysis. Manganese metal ion concentration was estimated by Atomic Absorption Spectroscopy.



Scheme 3: Incorporation of Manganese ion to PCS

3.3.2.2.1. Factors influencing incorporation of manganese ion

To investigate the factors influencing incorporation of manganese ion, PCS 2, which was obtained by the copolymerization of trichloromethylsilane and chlorodimethylvinylsilane, was selected as the polymer. The factors like nature of metal salt, duration of the experiment, swelling agent and the reaction temperature were considered for the study.

3.3.2.2.1.1. Nature of the metal salt

Manganese was incorporated into the polymers using manganese salts. Inorder to study the extent of metal ion immobilization on polycarbosilanes, different types of salts for each metal were taken in to consideration.

Table 5: Effect of nature of the manganese salt on metal intake capacity

Metal salt	Metal content (m. equiv./g)
Manganese chloride	1.21
Manganese acetate	3.10

In the case of manganese; it was found that manganese acetate gave good results and further experiments were conducted using manganese acetate for metal incorporation.

3.3.2.2.1.2. Effect of swelling agent on intake of metal ions

The reaction using polycarbosilanes are heterogeneous in nature taking place in two distinct phases. Compatibility of the two phases is an important factor which controls the extent of attachment of metal ions. Strong interaction with the metal ions in solution and the solid polymers must occur for the reaction to take place.

The extent of metal ion incorporation on polycarbosilane was studied in different solvents such as toluene, THF, xylene and ethanol. The polycarbosilane was suspended in different solvents and after swelling they were subjected to reaction with metal ion salt solution in ethanol. The metal intake capacity was determined in each case and the results obtained are given in table 6.

Table 6: influence of solvent on the metal intake capacity of PCS2*

Solvent	Metal content (m. equiv./g)
Toluene	3.10
THF	2.99
Xylene	3.05
Ethanol	2.50

*Temperature 323K, 12h

3.3.2.2.1.3. Metal intake capacity of PCS2 with time

To study the effect of reaction time on the incorporation of metal ions on polycarbosilane, the metal ion concentration was estimated in a constant interval of time. The reaction was done at 50^{o}C. It was observed that as the time increased from 6 h to 12 h a sharp increase in the metal content was obtained. But after 12 h no significant increase was noticed. So the duration for the reaction was selected as 12 h.

Table 7: Influence of duration of reaction on metal intake capacity*

Time (h)	Metal content (m. equiv./g)
6	2.11
12	3.10
18	3.25
24	3.93

*Temperature 323K, swelling agent toluene

3.3.2.2.1.4. Effect of temperature on the incorporation of metal ions

Temperature has a pronounced effect on the metal intake capacity. The macromolecular network with its functional groups produces additional segmental motion, with increase in temperature. As a result the metal ions are brought into closer contact with the reactive sites by penetration through the particles. Since the supporting macromolecular systems were thermally and mechanically stable, it could withstand changes in temperature. The influence of temperature on metal addition was studied at 303, 323 and 373 K. It was found that as the temperature was increased, the extent of metal intake by the polymer was increased. The experiments were done by taking toluene as swelling agent and for 12 h.

Table 8: Metal intake capacity of PCS 2 at various temperatures*

Temperature (K)	Metal content (m. equiv./g)
303	1.85
323	3.10
373	4.68

*Time 12h, swelling agent toluene.

From the above observations the optimized condition for incorporation of manganese ions was the use of manganese acetate as salt, toluene as swelling agent and the reaction temperature at 100°C for 12 h. All the polycarbosilanes were reacted with manganese.

3.3.2.2.2. Characterization of manganese attached polycarbosilane

3.3.2.2.2.1. Magnetic susceptibility measurements

The magnetic susceptibility of manganese ion attached polycarbosilanes was measured. The results are given in table 9.

Table 9: Susceptibility measurements of Mn-PCS

No.	M – PCS	Magnetic moment value (B.M.)
1	Mn – PCS1	5.50
2	Mn – PCS2	5.42
3	Mn – PCS3	5.44
4	Mn – PCS4	5.40
5	Mn – PCS5	5.20

From the magnetic susceptibility measurement results, it is clear that all the manganese ion incorporated polycarbosilane show paramagnetic nature and possess five unpaired electrons.

3.3.2.2.2.2. UV-Vis DRS analysis

The electronic spectra of manganese containing polycarbosilanes showed peaks around 416, 537, 632 and 690 nm. The peak around 416 nm corresponds to the charge transfer transition. The peak around 632 nm is due to the d-d transition.

3.3.2.2.2.3. FT-IR spectroscopy

In the infra red spectra of manganese containing polycarbosilanes a peak around 960 cm^{-1} was observed and the peak at 3448 cm^{-1} corresponding to Si-OH was diminished.

3.3.2.2.2.4. EPR spectroscopy

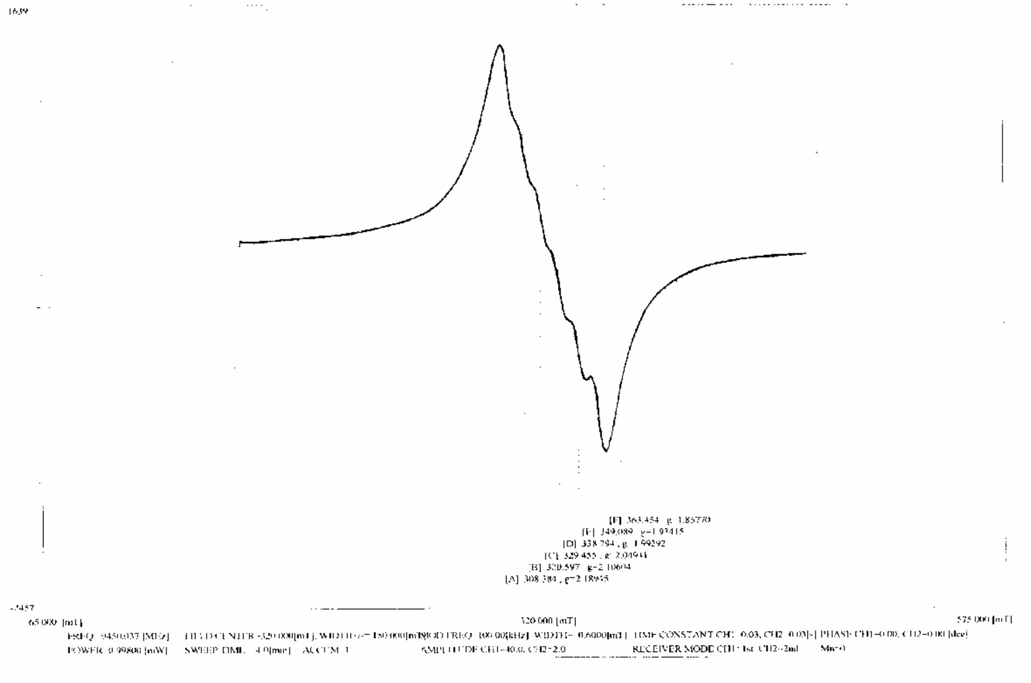


Figure 3: EPR spectrum of Mn-PCS 4

The solid state EPR spectrum of MnPCS4 is shown in fig 3. At an operating frequency of 9450 MHz, the Mn-PCS 4 exhibits six hyperfine splitting with g value centred at 2.02. The six hyperfine splitting due to electron-nuclear spin coupling is observed corresponding to the interaction of the electron spin with the nuclear spin (Mn, I=5/2). Here six hyperfine splitting lines corresponding to m_I = +5/2, +3/2, +1/2, ……, -1/2 are observed. The observed g value is close to the free electron value suggestive of the absence of spin orbit coupling in the ground state. The separation between two EPR signals gives a measure of 'A', hyperfine splitting constant. The magnitude of 'A' is determined by the nuclear magnetic moment and density of unpaired electron. g_{iso}= 2.02, A_{iso}= 11.01mT. This indicates the octahedral geometry around the metal ion.

3.3.2.2.2.5. ^{29}Si-NMR spectroscopy

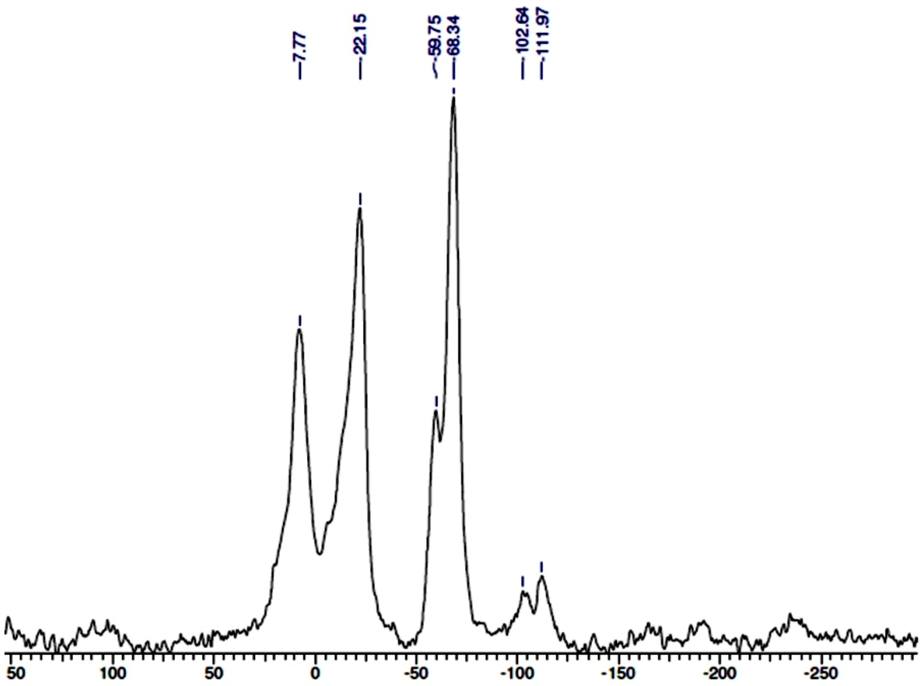


Figure 4: ^{29}Si CP-MAS NMR of Mn-PCS4

^{29}Si CP-MAS NMR spectrum of the manganese containing polycarbosilane is shown in figure 4. New peaks in the region around -102.64 and -111.97 ppm correspond to the Mn-O-Si linkage. It is seen that there is a total up field shift of the polycarbosilane peaks. Peak around -10.45 ppm has been shifted to -22.15 ppm and -48.77 ppm to -68.34 ppm and small peak around 18.79 ppm was shifted to 7.77 ppm. This trend is explained due to the presence of manganese metal attached to the polycarbosilane.

3.3.2.2.2.6. ^{13}C- NMR spectroscopy

^{13}C-NMR spectrum of Mn-PCS 4 was recorded. It is noticed that the peaks around 130 ppm and - 0.79 ppm. Peak at around -0.79 ppm is due to the polycarbosilane and the former one ie, 130 ppm corresponds to the peaks of acetate moiety. From this we can confirm the metal attachment to the polycarbosilane.

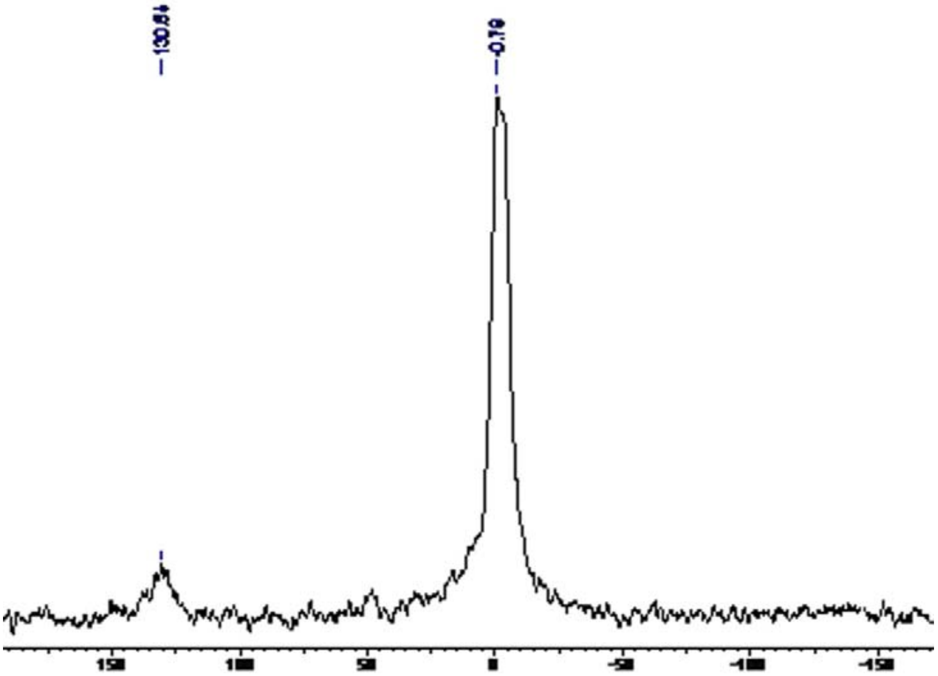


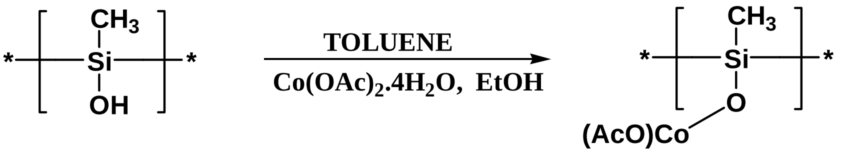
Figure 5: ^{13}C CP-MAS NMR spectrum of Mn PCS4

3.3.2.2.2.7. Thermogravimetric analysis

The thermogravimetric analysis of manganese containing polycarbosilane shows very small weight loss, which might be because of the evaporation of low molecular weight fractions of the polycarbosilane. It indicates the thermal stability of manganese containing polycarbosilane upto 1000°C.

3.3.2.3. Incorporation of cobalt ion on Polycarbosilane

Cobalt ion was attached to the polycarbosilane using its salts. Polycarbosilane was stirred in toluene for 24 h (to swell). Metal salt dissolved in ethanol was added to it and stirred for 12 h. It was filtered and washed with methanol in a soxhlet extractor and dried.



Scheme 4: Cobalt ion incorporation on PCS

3.3.2.3.1. Factors influencing metal incorporation

To investigate the factors influencing metal incorporation, PCS 2, which is a copolymer of trichloromethylsilane and chlorodimethylvinylsilane, was selected as the polymer. The factors like nature of metal salt, duration of the experiment, swelling agent and the reaction temperature were considered for the study. The metal content of the cobalt attached polycarbosilane was estimated using AAS.

3.3.2.3.1.1. *Nature of the metal salt*

Cobalt ion was attached to the polycarbosilane using corresponding salts. Inorder to study the extent of metal intake by polycarbosilanes, different cobalt salts were taken in to consideration. The results are listed in table 10.

Table 10: Effect of nature of the cobalt salt on metal intake capacity

Metal salt	**Metal content (m. equiv./g)**
Cobalt chloride	0.47
Cobalt acetate	1.23

From the AAS results, cobalt acetate was chosen as the salt for cobalt ion incorporation to polycarbosilane.

3.3.2.3.1.2. *Effect of swelling agent on intake of metal*

The reaction involving polycarbosilanes are heterogeneous in nature taking place in two different phases. Even though the polycarbosilane appears to be a solid insoluble in solvents; virtually it behaves as a gel which expands to a large extent in good solvents and the functional groups (OH) attached to the polycarbosilane will be exposed for the reaction. Strong interaction with the metal ions in solution and the solid polymer must occur for the reaction to take place.

The extent of cobalt ion incorporation on polycarbosilane was studied in different solvents such as toluene, THF, xylene and ethanol. The polycarbosilane was suspended in different solvents and after swelling they were subjected to reaction with ethanolic solution of metal salt. The metal intake capacity was determined in each case using AAS and the results obtained are given in table 11.

Table 11: Metal intake capacity of PCS2*

Solvent	Metal content (m. equiv./g)
Toluene	1.23
THF	0.83
Xylene	1.01
Ethanol	0.59

*Temperature 323K, 12h

3.3.2.3.1.3. Metal intake capacity of PCS2 with time

Inorder to study the effect of reaction time on the incorporation of metal ions on polycarbosilane, reaction for the metal incorporation of cobalt ion on PCS2 were conducted using cobalt acetate at 50°C. The metal ion concentration was estimated by AAS in a constant interval of time. The results are listed in table 12.

Table 12: Metal intake capacity of PCS2 with time*

Time (h)	Metal content (m. equiv./g)
6	0.52
12	1.23
18	1.33
24	1.54

*Temperature 323K, swelling agent toluene

It is observed that as the time increases from 6 h to 12 h a sharp increase in the metal content was obtained. But after 12 h no significant increase was observed. So the reaction time was selected as 12 h.

3.3.2.3.1.4. Effect of temperature on metal incorporation

With increase in temperature, the macromolecular network with its functional groups produces additional segmental motion. As a result, the metal ions were brought into closer contact with the reactive sites by penetration through the particles. Since the supporting macromolecular system was thermally and mechanically stable, it could withstand changes in temperature. The influence of temperature on metal addition was studied at 303, 323 and 373 K. The metal content estimated by AAS is listed in table 13.

Table 13: Metal intake capacity of PCS 2 at various temperatures*

Temperature (K)	Metal content (m. equiv./g)
303	0.52
323	1.23
373	2.37

*Time 12h, swelling agent toluene

It was found that as the temperature was increased, the extent of metal intake by the polymer was also increased. So 373 K was selected as the optimum temperature for cobalt ion incorporation.

From the above observations the optimized condition for incorporation of cobalt ion was the use of cobalt acetate as salt, toluene as swelling agent and the reaction temperature at 100^{o}C for 12 h. All the polycarbosilanes were reacted with cobalt ion and were characterized.

3.3.2.3.2. Characterization of cobalt ion attached polycarbosilane

The cobalt ion incorporated polycarbosilane was characterized by UV-Vis DRS analysis, FT-IR spectroscopy, magnetic susceptibility measurement, TG-DTA and surface area analysis. Cobalt metal content was estimated by Atomic Absorption Spectroscopy.

3.3.2.3.2.1. Magnetic susceptibility measurements

Magnetic susceptibility measurements show that the cobalt incorporated polycarbosilanes are diamagnetic in nature

3.3.2.3.2.2. Infra red spectroscopy

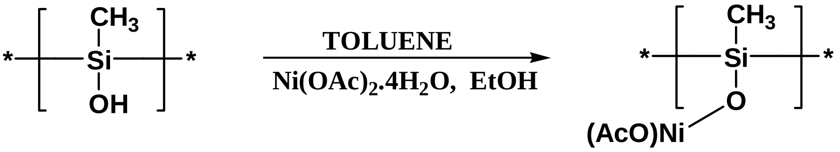
The infra red spectra of cobalt incorporated polycarbosilane showed a peak around 970 cm^{-1}. And the peak corresponding to Si-OH was diminished.

3.3.2.3.2.3. Thermogravimetric analysis

The thermogravimetric analysis of cobalt ion attached polycarbosilane showed very small weight loss, which might be because of the evaporation of low molecular weight fractions of the polycarbosilane. It indicates the thermal stability of cobalt incorporated polycarbosilane upto 1000°C.

3.3.2.4. Incorporation of Nickel ion on Polycarbosilane

To attach nickel ion on polycarbosilane using corresponding salts, polymer was stirred in toluene for 24 h (to swell). The metal salt was added to it as an ethanolic solution and stirred for 12 h. It was filtered and washed with methanol in a soxhlet extractor and dried. The nickel attached polycarbosilane was green in colour. The metal ion content was estimated by AAS.



Scheme 5: Nickel ion incorporation on PCS

3.3.2.4.1. Factors influencing metal incorporation

To study the factors influencing the metal ion incorporation, PCS 2, which is the copolymer of trichloromethylsilane and chlorodimethylvinylsilane, was selected as the polymer. The factors like nature of metal salt, duration of the experiment, swelling agent and the reaction temperature were considered for the study.

3.3.2.4.1.1. Nature of the metal salt

Nickel ion was incorporated into the polycarbosilane using various nickel salts. Inorder to study the extent of metal ion intake by polycarbosilane, different types of salts of nickel were taken in to consideration. The metal content was estimated in each case and the results are given in table 14.

Table 14: Effect of nature of the nickel salt on metal intake capacity

Metal salt	Metal content (m. equiv./g)
Nickel chloride	0.58
Nickel acetate	1.51

From the results of atomic absorption spectroscopy, acetate salt was chosen for nickel ion incorporation on polycarbosilane.

3.3.2.4.1.2. Effect of swelling agent on intake of metal

Even though the polycarbosilane appears to be a solid insoluble in solvents; it behaves as a gel which swells in good solvents and the functional groups (OH) attached to the polymer is now exposed. Strong interaction with the metal ions in solution and the solid polymers must occur for the substitution reaction to take place.

The metal intake capacity of polycarbosilane was studied in different solvents such as toluene, THF, xylene and ethanol. The PCS 2 was suspended in different solvents and after swelling they were subjected to reaction with ethanolic solution of nickel acetate for 12 h at 50 ^{o}C. The metal intake capacity was determined in each case and the results obtained are given in table 15.

Table 15: Metal intake capacity of PCS2*

Solvent	**Metal content (m. equiv./g)**
Toluene	1.51
THF	0.91
Xylene	1.50
Ethanol	0.89

*Temperature 323K, 12h.

3.3.2.4.1.3. Metal intake capacity of PCS2 with time

To study the influence of reaction time in the nickel ion incorporation of the polycarbosilane the metal ion concentration was estimated in a constant interval of time. The reaction was done at 50^{o}C. The metal content was estimated using AAS and the results are listed in table 16.

Table 16: Metal intake capacity of PCS2 with time*

Time (h)	Metal content (m. equiv./g)
6	1.21
12	1.51
18	1.62
24	1.84

*Temperature 323K, swelling agent toluene

We can notice that as the time increases from 6 h to 12 h a sharp increase was observed in the metal content. But after 12 h significant increase was not observed. Hence 12 h was selected as the optimum reaction time.

3.3.2.4.1.4. Effect of temperature on incorporation of nickel ion

Temperature has a pronounced effect on metal intake capacity of polymers. Since the macromolecular network with its functional groups produces additional segmental motion with increase in temperature, the metal ions are brought into closer contact with the reactive sites by penetration through the particles. As the polycarbosilanes were thermally and mechanically stable, it could withstand changes in temperature. The influence of temperature on metal addition was studied at 303, 323 and 373 K. The result of estimation of metal content is given in table 17.

Table 17: Metal intake capacity of PCS 2 at various temperatures*

Temperature (K)	Metal content (m. equiv./g)
303	0.54
323	1.51
373	3.37

*Time 12h, swelling agent toluene.

It was observed that as the temperature was increased, the metal intake capacity of the polycarbosilane was also increased.

From the above observations, the optimized condition for incorporation of nickel ion was the use of nickel acetate as salt, toluene as swelling agent and the reaction temperature at 100°C for 12 h. All the polycarbosilanes were reacted with nickel ions and were characterized.

3.3.2.4.2. Characterization of nickel ion attached polycarbosilane

The nickel ion containing polycarbosilane was characterized by UV-Vis-DRS analysis, FT-IR spectroscopy, magnetic susceptibility measurement, TG-DTA and surface area analysis. Nickel ion content was estimated by Atomic Absorption Spectroscopy.

3.3.2.4.2.1. Magnetic susceptibility measurements

Magnetic susceptibility measurements showed that the nickel incorporated polycarbosilanes are diamagnetic in nature. This may be because of their square planar geometry.

3.3.2.4.2.2. Infra red spectroscopy

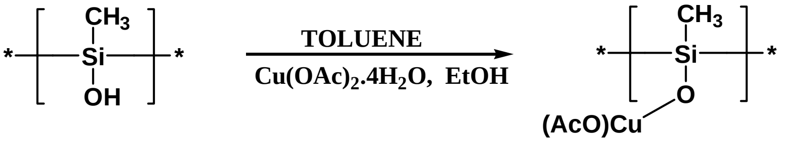
The FT-IR spectra of the Ni-PCSs were recorded. They showed the peak corresponding to Si-O-Ni at 908 cm^{-1}.The spectra showed a broad band at 1025 cm^{-1} corresponding to Si-O vibration.

3.3.2.4.2.3. Thermogravimetric analysis

The thermogravimetric analysis of nickel incorporated polycarbosilane showed very small weight loss, which might be because of the evaporation of low molecular weight fractions of the polycarbosilane. It indicates the thermal stability of nickel ion attached polycarbosilane upto 1000°C.

3.3.2.5. Incorporation of Copper ion on Polycarbosilane

Copper ion was incorporated into the polycarbosilanes using their corresponding salts. Polymer was stirred in toluene for 24 h (to swell). Copper salt dissolved in ethanol was added to it and stirred for 12 h. It was filtered and washed with methanol in a soxhlet extractor and then dried. The copper ion attached polycarbosilane was green in colour.



Scheme 6: Copper ion incorporation on PCS

3.3.2.5.1. Factors influencing incorporation of copper ion

To investigate the factors influencing copper ion incorporation, PCS 2, which is the copolymer of trichloromethylsilane and chlorodimethylvinylsilane, was selected as the polymer. The factors like nature of metal salt, reaction time, swelling agent and the reaction temperature were considered for the study. The metal content was estimated by AAS technique.

3.3.2.5.1.1. Nature of the metal salt

Copper ion was incorporated into the polymers using various copper salts. Inorder to study the extent of metal intake by polycarbosilane, different copper salts were taken in to consideration. The results are shown in table 18.

Table 18: Effect of nature of the copper salt on metal intake capacity

Metal salt	**Metal content (m. equiv./g)**
Copper chloride	1.16
Copper sulphate	1.26
Copper acetate	4.11

The results indicate higher metal intake of PCS 2 when acetate salt was used than in the case of sulphate and chloride. Hence it was selected as the salt for copper ion incorporation.

3.3.2.5.1.2. Effect of swelling agent on intake of metal

The reaction using polycarbosilanes are taking place in two distinct phases. Compatibility of the two phases is an important factor which controls the extent of metal intake by the polymer. Strong interaction with the metal ions in solution and the solid polymers must occur for the reaction to take place.

The extent of metal intake capacity of polycarbosilane was studied in different solvents such as toluene, THF, xylene and ethanol. The PCS 2 was suspended in different solvents and after swelling they were subjected to reaction with copper acetate solution in ethanol. The metal intake capacity was determined in each case and the results obtained are given in table 19.

Table 19: Metal intake capacity of PCS2*

Solvent	Metal content (m. equiv./g)
Toluene	4.11
THF	3.94
Xylene	4.10
Ethanol	2.89

*Temperature 323K, 12h

The AAS results indicate that the toluene is a better solvent for the reaction of copper ion incorporation on polycarbosilane.

3.3.2.5.1.3. Metal intake capacity of PCS2 with time

To study the effect of reaction time in the copper ion incorporation of the polycarbosilane, the reaction was conducted using toluene as swelling agent and copper acetate as salt at 50°C. The metal ion concentration was estimated in a constant interval of time.

Table 20: Metal intake capacity of PCS2 with time*

Time (h)	Metal content (m. equiv./g)
6	2.65
12	3.13
18	3.53
24	4.14

*Temperature 323K, swelling agent toluene

It was observed that as the time increases from 6 h to 12 h a sharp increase in the metal content was observed. But after 12 h no such sudden increase has taken place. So we have selected the time for the experiment as 12 h.

3.3.2.5.1.4. Effect of temperature on incorporation of copper ion

Temperature has a significant effect on metal ion incorporation. As the temperature increases, the polymeric network produces additional segmental motion. As a result the metal ions are brought into closer contact with the reactive sites by penetration through the particles. Since the supporting macromolecular system was thermally and mechanically stable, it could withstand changes in temperature. The influence of temperature on metal addition was studied at 303, 323 and 373 K. The AAS results are listed in table 21.

Table 21: Metal intake capacity of PCS 2 at various temperatures*

Temperature (K)	**Metal content (m. equiv./g)**
303	2.10
323	4.11
373	5.54

*Time 12h, swelling agent toluene

It was found that as the temperature was increased, the metal intake capacity of the polymer was also increased. 373 K was selected as the optimum temperature for the reaction.

From the above observations, the optimized condition for metal incorporation was the use of copper acetate as salt, toluene as swelling agent and the reaction temperature at 100°C for 12 h. All the polycarbosilanes were reacted with copper salts and were characterized.

3.3.2.5.2. Characterization of Copper attached polycarbosilane

The metal containing polycarbosilane was characterized by UV-Vis-DRS analysis, FT-IR, ^{29}Si-CP-MAS NMR spectroscopy, magnetic susceptibility measurement, EPR analysis, TG-DTA, and surface area analysis. Copper metal was estimated by Atomic Absorption Spectroscopy.

3.3.2.5.2.1. UV-Vis DRS analysis

The electronic spectra of the copper containing polycarbosilanes showed peaks around 414 nm, 636 nm and 689 nm. Peak around 414 nm indicated the charge transfer transition of the metal ion and the latter peaks correspond to the d-d transitions in them.

3.3.2.5.2.2. FT-IR spectroscopy

The FT-IR spectra of the Cu-PCSs were recorded. They showed the peak corresponding to Si-O-Cu at 949 cm^{-1}.The spectrum showed a broad band at 1025 cm^{-1} corresponding to Si-O vibration.

3.3.2.5.2.3. Magnetic susceptibility measurements

The magnetic susceptibility of copper ion attached polycarbosilanes was measured. The results are given in table 22.

Table 22: Magnetic susceptibility values of Cu-PCS

No.	M – PCS	Magnetic moment value (B.M.)
1	Cu – PCS1	1.86
2	Cu – PCS2	1.84
3	Cu – PCS3	1.88
4	Cu – PCS4	1.80
5	Cu – PCS5	1.87

From the magnetic susceptibility measurement results, it is clear that all the copper ion incorporated polycarbosilane showed paramagnetic nature and possessed one unpaired electron.

3.3.2.5.2.4. EPR Spectroscopy

EPR spectrum of Cu-PCS 4 is shown in fig 6. The copper (II) ion, with d^9 configuration, has an effective spin of S = 1/2 and is associated with a spin angular momentum, ms= ±1/2, leading to a doubly degenerate spin state in the absence of a magnetic field. Operating frequency of 9450 MHz, we get an EPR signal at around 319 mT. Diphenyl picryl hydrazide (DPPH) which has a ‘g’ value of 2.0036 is used as a calibrant in order to measure the resonance field H of the sample when ν is known.

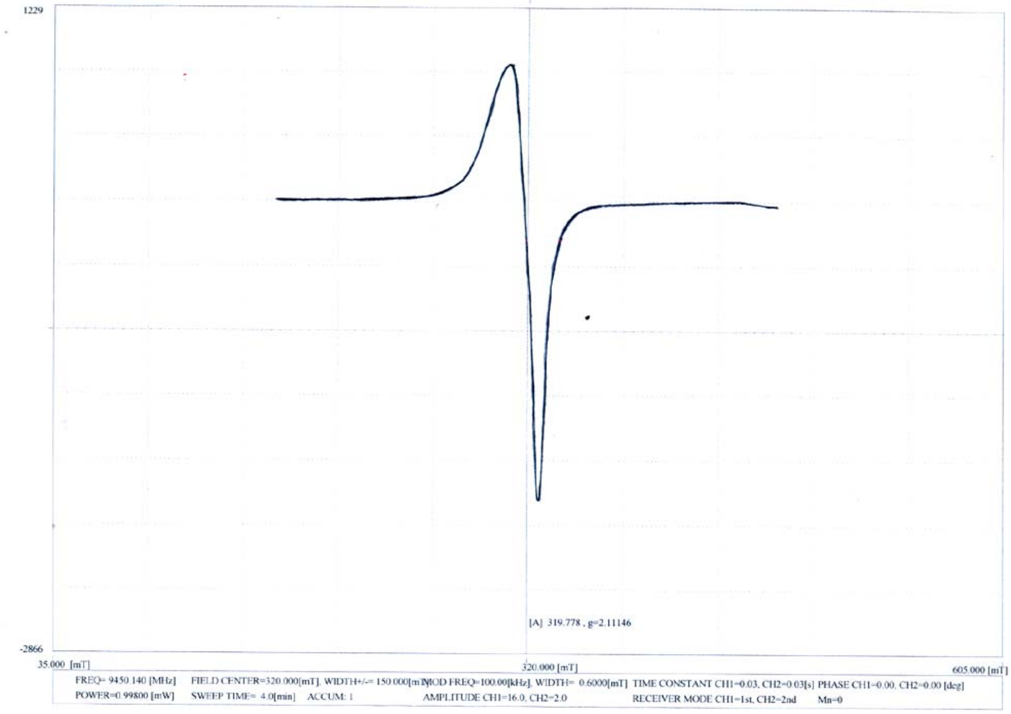


Figure 6: EPR spectrum on Cu-PCS 4

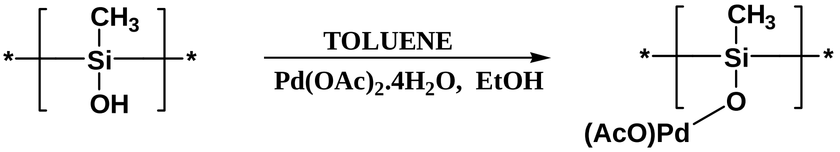
From the spectrum it is clear that it is an isotropic spectrum and $g_{iso} = 2.11$.

3.3.2.5.2.5. Thermogravimetric analysis

The thermogravimetric analysis of copper incorporated polycarbosilanes showed very small weight loss, which might be because of the evaporation of low molecular weight fractions of the polycarbosilane. It indicates the thermal stability of copper incorporated polycarbosilane upto 1000°C.

3.3.2.6. Incorporation of Palladium ion on Polycarbosilane

Palladium ion was incorporated into the polycarbosilane using its salt. From the surface area analysis, it was clear that PCS 4 which is a copolymer of of trichloromethylsilane and trimethoxyvinylsilane, posess high surface area and is measoporous in nature. Hence PCS 4 was selected as the polymer for palladium ion incorporation. Polymer was stirred in toluene for 24 h (to swell). Then metal salt dissolved in ethanol was added to it and stirred for 12 h. The reaction mixture was filtered and washed with methanol in a soxhlet extractor and dried. The palladium ion attached polycarbosilane was black in colour.



Scheme 7: Palladium ion incorporation on PCS 4

3.3.2.6. Factors influencing incorporation of palladium ion

From the observations of incorporation of various metal ions on polycarbosilanes, the optimum condition for metal incorporation was chosen as the use of toluene as swelling agent and the reaction temperature at 100°C for 12 h. Palladium ion content was estimated using AAS.

3.3.2.6.1. Nature of the metal salts

Inorder to study the effect of metal ion intake on polycarbosilane, different types of palladium salts were taken in to consideration.

Table 23: Effect of nature of palladium salt on metal intake capacity

Metal salt	Metal content (m. equiv./g)
Palladium chloride	1.66
Palladium acetate	5.20

From the results obtained form AAS; palladium acetate was selected as salt for palladium ion incorporation.

3.3.2.6.2. Characterization of Palladium attached polycarbosilane

The metal containing polycarbosilane was characterized by UV-Vis DRS analysis, FT-IR, magnetic susceptibility measurement, TG-DTA surface area analysis. Palladium metal ion concentration was estimated by Atomic Absorption Spectroscopy.

3.3.2.6.2.1. UV-Vis DRS analysis

Electronic spectrum showed peaks at 637 nm and 717 nm. The magnetic susceptibility result indicates the diamagnetic nature of the Pd-PCS 4. Thus the geometry around metal ion is suggested as square planar.

3.3.2.6.2.2. FT-IR Spectroscopy

The FT-IR spectrum of the Pd-PCS4 was recorded. It showed the peak corresponding to Si-O-Pd at 980 cm^{-1}.The spectrum showed a broad band at 1025 cm^{-1} corresponding to Si-O vibration.

3.3.2.6.2.3. Magnetic susceptibility measurement

The magnetic susceptibility measurement gave the value which is approximately equal to zero. The result shows that the palladium incorporated polycarbosilane is diamagnetic.

3.3.2.6.2.4. Thermogravimetric analysis

The thermogravimetric analysis of palladium incorporated polycarbosilane shows very small weight loss, which might be because of the evaporation of low molecular weight fractions of the polycarbosilane. It indicates the thermal stability of palladium incorporated polycarbosilane upto 1000^{o}C.

The metal ion incorporation on five polycarbosilanes were done successfully, the reaction conditions for the metal incorporation were by taking toluene as swelling agent and reaction were conducted at 100°C and for 12h. The results of the metal incorporation on polycarbosilanes are listed in table 24.

Table 24: Results of metal ion incorporation on PCS

Polymer	Titanium	Manganese	Cobalt	Nickel	Copper	Palladium
PCS 1	3.21	3.33	0.89	0.75	3.35	-
PCS 2	4.43	4.68	2.37	3.37	5.54	-
PCS 3	4.21	4.32	2.11	2.96	4.5	-
PCS 4	5.43	4.35	1.52	2.32	5.54	5.20
PCS 5	0.63	0.51	0.21	0.27	0.4	-

3.3.2.6.2.5. Surface area analysis

Surface area analysis of metal incorporated polycarbosilanes was done. The analysis was conducted only for metal incorporated to polycarbosilane 4; since the polycarbosilane 4 was found to be with high surface area in the BET experiment. The results of surface area analysis are entered in table 3.25.

Table 3.25: Surface area of metal ion attached PCS 4

Sample	Surface area (m^2/g)	
	BET	**Langmuir**
PCS 4	679	1171
Ti PCS 4	580	990
Mn PCS 4	573	988
Co PCS 4	614	1025
Ni PCS 4	603	1004
Cu PCS 4	556	956
Pd PCS 4	311	480

3.4. Conclusion

The polycarbosilane supported metal ions of Ti (IV), Mn (II), Co (II), Ni (II), Cu (II) and Pd (II) were prepared from corresponding salts. The metal attached polycarbosilanes were characterized using various analytical methods. The spectroscopic techniques used are FT-IR, UV-Vis DRS, ^{29}Si-CP-MAS NMR, ^{13}C CP-MAS NMR, EPR spectroscopy and TG/DTA, magnetic susceptibility measurements, BET surface area analysis and AAS/ICP-AES. Factors influencing the metal ion incorporation were studied in detail.

3.5. Experimental

3.5.1. Preparation of hydroxyl substituted polycarbosilanes

Inorder to substitute the chloride groups with hydroxyl group the polycarbosilanes were refluxed in water for 24h. It was then cooled and the suspension obtained was filtered and dried.

3.5.2. Metal Incorporation on Polycarbosilanes

3.5.2.1. Titanium ion immobilization on polycarbosilanes

1 g of polycarbosilane was stirred in toluene for 16 h to swell. Titanium isopropoxide (1.79 mL, 6 mmol) was added to the swollen polymers and again stirred for another 12 h. The metal incorporated polycarbosilanes were filtered, washed with methanol in a soxhlet and dried.

3.5.2.2. Manganese ion immobilized polycarbosilane

1 g of polycarbosilane was stirred for 12 h in toluene to swell. Manganese acetate (1.47 g, 6 mmol) as a solution in ethanol was added drop wise to the swelled polycarbosilane and was stirred for 12h. The reaction mixture was filtered, washed in a soxhlet with methanol and dried.

3.5.2.3. Cobalt ion immobilized polycarbosilane

1 g of the polycarbosliane was stirred in toluene to swell. Cobalt acetate (1.49 g, 6 mmol) solution in ethanol was added drop wise and was stirred for 12h. The reaction mixture was filtered, washed in a soxhlet with methanol and dried.

3.5.2.4. Nickel ion immobilized polycarbosilane

1 g of the polycarbosilane was stirred in toluene to swell. Nickel acetate (1.49 g, 6 mmol) as ethanol solution was added drop wise and was stirred for 12h. The reaction mixture was filtered, washed in a soxhlet with methanol and dried.

3.5.2.5. Copper ion immobilized polycarbosilane

1 g of the polycarbosilane was stirred in toluene to swell. Copper acetate (1.2 g, 6 mmol) solution in ethanol was added drop wise and was stirred for 12h. The reaction mixture was filtered, washed in a soxhlet with methanol and dried.

To study the effect of reaction time in the copper ion intake by the polycarbosilane, the reaction was conducted using toluene as swelling agent and copper acetate as salt at 50^{o}C. The metal ion concentration was estimated in a constant interval of time.

3.5.2.6. Palladium ion immobilized polycarbosilane

1 g of PCS 4 was stirred in toluene to swell. Ethanolic solution of palladium acetate (1.35g, 6 mmol) was added drop wise and was stirred for 12h. The reaction mixture was filtered, washed in a soxhlet with methanol and dried.

To study the effect of reaction time on the metal intake by the polymer, the polymer was allowed to react with metal ion solution in ethanol, in the case of titanium the isopropoxide salt was used as directly, at various intervals of time. The polymer was filtered after the fixed intervals and the metal intake was estimated.

To study the effect of swelling agent, the polymer was allowed to swell in different solvents for 12 h. then the metal ion solution in ethanol, in the case of titanium the isopropoxide salt was used as directly, was added to it and stirred for 12 h. the best swelling agent was selected as toluene which gave the maximum metal incorporation.

The metal estimation was done using Atomic Absorption Spectroscopy; the titanium metal estimation was done by ICP-AES.

The metal containing polycarbosilanes were characterized by FT-IR, ^{29}Si-CP-MAS NMR, TG-DTA, AAS/ ICP-AES and surface area analysis.

3.6. References

1 Tsirlin, A.M.; Shcherbakova, G.I.; Florina, E.K.; Popova, N.A.; Gubin, S.P.; Moroz, E.M.; Riedel, R.; Kroke, E.; Steen, M. *J. Eur. Ceram. Soc.* **2002**, *22*, 2577.

2 Dvornic, P. R.; Owen, M. J. *Silicon-Containing Dendritic Polymers Advances in Silicon Science,* **2009**, *2*, USA, Springer.

3 Chan, W.Y.; Clendenning, S. B.; Berenbaum, A.; Lough, A. J.; Aouba, S.; Ruda, H. E. Manners, I. *J Am Chem Soc*. **2005**, *127*, 1765.

4 Oyamada, H.; Akiyama, R.; Hagio, H.; Naito, T.; Kobayashi, S. *Chem. Commun.* **2006**, *41*, 4297.

5 Rushkin, I. L.; Shen, Q.; Lehman, S. E.; Interrante, L. V. *Macromolecules*, **1997**, *30*, 3141.

6 Peterson, W. R., Jr.; Arkles, B. C. U.S. Patent 4,276,424, **1981**.

7 Interrante, L. V.; Lu, N. US Patent 6,809,041, **2004**. Rathore, J. S.; Interrante, L. V.; Dobois, G. *Adv. Funct. Mater.* **2008**, *18*, 1.

8 Houser, E. J.; Mc Gill, R. A. US Patent 7,078,548, **2006**.

9 Ganicz, T.; Stanczyk, W. A.; Chmielecka, J.; Kowalski, J. *Polym. Int.*, **2009**, *58*, 248.

10 Greenberg, S.; Clendenning, S. B.; Liu, K.; Manners, I. *Macromolecules*, **2005**, *38*, 2023.

11 Ganicz, T.; Stanczyk, W. A.; Gladkova, N. K.; Śledzińska, I. *Macromolecules*, **2000**, *33*, 289.

12 Song, Y. C.; Hasagawa, Y.; Yang, S. J.; Sato, M. *J. Mater. Sci.* **1988**, 23, 1911.

13 Laine, R. M.; Babonneau, F. *Chem. Mater.* **1993**, 5, 260.

14 Gubin, S. P.; Moroz, E. M.; Boronin, A. I.; Kriventsov, V. V.; Zyuzin, D. A.; Popova, N. A.; Florina, E. K.; Tsirlin, A. M. *Mendeleev Communications*, **1999**, *9*, 59.

15 Kulbaba, K.; Cheng, A.; Bartole, A.; Greenberg, S.; Resendes, R.; Coombs, N.; Safa-Sefat, A.; Greedan, J. E.; Stover, H. D. H.; Ozin, G. A.; Manners, I. *J. Am. Chem. Soc.* **2002**, *124*, 12522.

16 de Miguel, Y. R.; Brule´, E.; Margue, R. C. *J. Chem. Soc., Perkin Trans. 1* **2001**, 3085.

17 Ikegami, S.; Hamamoto, H. *Chem. Rev.* **2009**, *109,* 583.

18 da Cruz, R. S., de Souza e Silva, J. M., Arnold, U., Sercheli, M. S. And Schuchardt, U. *J. Braz. Chem. Soc.* **2002**, *13*, 170.

19 Ebitani, K.; Motokura, K.; Mori, K.; Mizugaki, T.; Kaneda, K. *J. Org. Chem.* **2006**, *71*, 1449.

20 Reger, T. S.; Janda, K. D. *J. Am. Chem.* **2000**, *122*, 6929.

21 Nair, V. A.; Sreekumar, K. *Curr. Sci.* **2001**, *81*, 194.

22 Nair, V. A.; Sreekumar, K. *J. Polym. Mater.* **2002**, *19*, 155.

23 Nair, V. A.; Sumi, M.; Sreekumar, K. *Proc. Indian Acad. Sci. (Chem. Sci.)* **2002**, *114,* 481.

24 Nair, V. A.; Sumi, M.; Sreekumar, K. *Designed Monomers and Polymers* **2003**, *6*, 81.

25 Krawiec, P.; Kockrick, E.; Borchardt, L.; Geiger, D.; Corma, A.; Kaskel, S. *J. Phys. Chem, C.*, **2009**, *113*, 7755.

26 Oyamada, H.; Akiyama, R.; Hagio, H.; Naito, T.; Kobayashi, S. *Chem. Commun.*, **2006**, *31*, 5609.

27 Schilling, C. L.; Hudson, C. O.; William, T. C.; Wesson, J. P. US Patent, 4,497,787, **1985**.

28 Novak, I.; Huang, W.; Luo, L.; Huang, H. H.; Ang, H. G.; Zybill, C. E. *Organometallics*, **1997**, *16*, 1567

29 Lu, J.; Toy, P. H. *Chem. Rev.* **2009**, *109,* 815

30 Buchmeiser, M. R. *Chem. Rev.* **2009**, *109,* 303.

31 Trindade, A. F.; Gois, P. M. P.; Afonso, C. A, M. *Chem. Rev.* **2009**, *109,* 418.

Chapter 4

STUDY OF CATALYTIC ACTIVITY OF METAL CONTAINING POLYCARBOSILANES

Contents

4.1. Introduction

Evolution of clean and environmentally benign chemical processes using less hazardous catalysts has become a primary goal in synthetic organic chemistry[1,4]. Running a reaction under heterogeneous condition is more promising, since it involves the facile recovery and reuse of the expensive catalyst[2]. The development of supported catalysts for use in environmentally friendly or green solvents, as part of the drive towards developing green chemistry protocol, is also an idea that is getting more acceptance[2-5].

Recent interest in the development of environmentally benign synthesis has evoked a renewed interest in developing polymer bound metal catalysts and reagents for organic synthesis, that maintain high activity and selectivity. Catalysis and reagents immobilized on a range of insoluble supports have been utilised and reported since the late 1960's[1-10]. The immobilization of transition metal ions on polymer supports offers a number of advantages over solution phase chemistry. In an ideal case, the supported complexes can be recovered from reaction mixtures by simple filtration, they do not contaminate the product solution, they can be recycled, and they can help increase in selectivity. Such immobilization also enables the use of high concentration of reagents to drive reaction to completion. Another advantage is the unique microenvironment created for the reactants within the polymer support enabling increased reaction rate.

The development of polymer supported catalysts can be considered as an advancement for attaining one of the major goals of 'green chemistry', ie, to facilitate efficient recovery of the catalyst from the reaction products, there by reducing inorganic waste[2-5].

By introducing transition metal ions to polycarbosilanes, we can create functional polymers with properties as preceramic and with catalytic activity. Relatively few examples of metal- functionalized polycarbosilanes have been reported.[11,12] In a reaction, the functionalized macromolecules with bound catalytic centers surrounded by solvents fulfil the function of isolated micro reactors. The high surface area of the polycarbosilane increases the rate of the reaction.

The present chapter discusses about the investigation of the catalytic activity of polycarbosilane supported transition metal ions. The reactions studied are 1) Biginelli reaction, 2) Knoevenagel condensation reaction, 3) Mannich reaction and 4) Heck reaction. The reaction conditions were optimized and recycling of catalysts were studied.

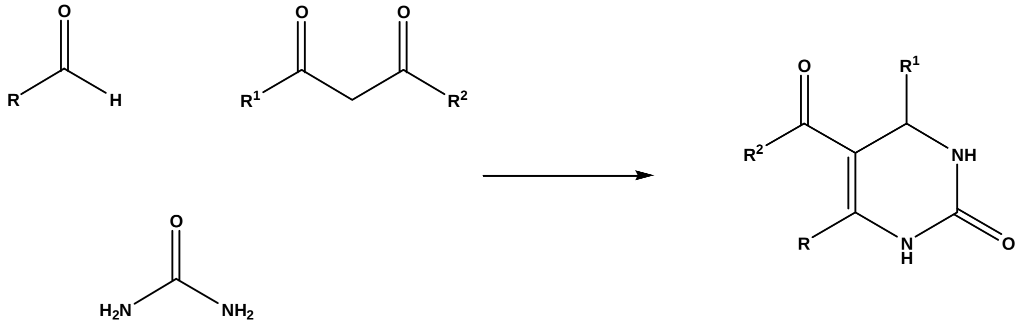
4.2. Results and Discussion

Multicomponent reactions (MCRs) are of increasing importance in organic and medicinal chemistry. Multiple-component condensation (MCC) where three or more reactants combine to afford a new core structure possessing the molecular features of its composite building blocks is a powerful method for the preparation of molecular diversity. Here three or more reactants are combined in a single vessel to generate new molecules that contain portions of each reactant, undoubtedly maintain great importance in organic synthesis. It also enables molecular diversity required in the discovery of new lead compounds.

4.2.1. Biginelli Reaction

One of many examples of a three component condensation (3CC), Biginelli reaction, brings together ureas, aldehydes and *β*-ketoesters, to afford functionalized pyrimidinones as the core structure. The first reported synthesis of 3,4-dihydropyrimidine-2-ones using a multicomponent reaction was described by Biginelli in 1893. The reaction was conducted in an acidic ethanolic solution.

The Biginelli reaction has been known as an efficient one-pot reaction protocol to prepare 3, 4-dihydropyrimidin-2(1*H*)-one (DHPM) derivatives[13-16]. Traditionally, Brønsted acids are primarily used for promoting the Biginelli reaction. DHPM derivatives are known as interesting heterocyclic scaffolds for drug research. Such heterocycles show a wide scope of important pharmacological properties and make up a large family of medicinally relevant compounds[14-16]. These molecules have been shown to elicit calcium channel modulatory activity, inhibit platelet activating factor, and selectively antagonize the human α_{1A} receptors, to name a few.

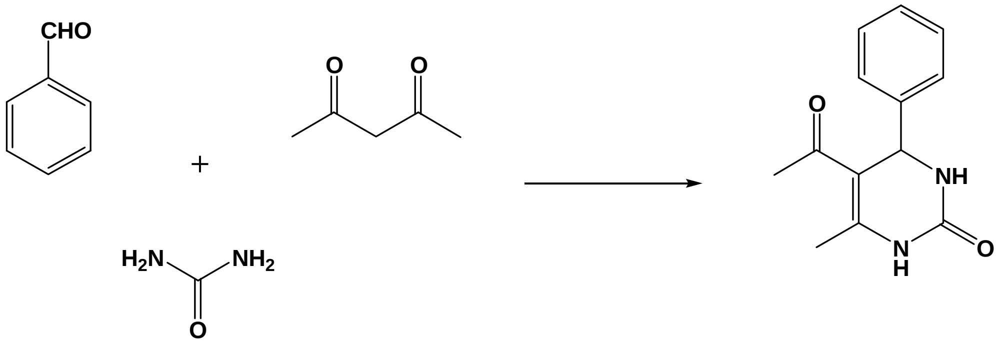


Scheme 1: General scheme for Biginelli reaction

A mixture of diketone, aldehyde and urea in equal molar concentration in ethanol was added to the metal containing polycarbosilane (5 mol %) and was heated under reflux for 8 h. The % conversion of each of the products were analyzed by HPLC with a solvent ratio (CH_3OH:H_2O) of 75:25.

4.2.1.1. Influence of metal ion attached polycarbosilanes in Biginelli reaction

To investigate the effect of polycarbosilanes which were used as supports for metal ions, the reaction was conducted with metal ions which were attached to different polycarbosilane. The reaction between benzaldehyde, acetyl acetone and urea according to scheme 2 and all the five polycarbosilanes attached with metal ions were considered as catalyst for the reaction.



Scheme 2: Biginelli reaction with benzaldehyde, acetyl acetone and urea

Biginelli reaction of benzaldehyde, acetyl acetone and urea was done in the presence of 5 mol % metal incorporated polycarbosilane as catalyst and ethanol as solvent under reflux condition for 8h. The results of the study are given in table 1.

Table 1: Biginelli reaction: influence of the nature of PCS*

Catalyst	Conversion (%)
Ti PCS1	78
Ti PCS2	76
Ti PCS3	74
Ti PCS4	87
Ti PCS5	73
Mn PCS1	80
Mn PCS2	76
Mn PCS3	74
Mn PCS4	86
Mn PCS5	73
Co PCS1	80
Co PCS2	75
Co PCS3	73
Co PCS4	87
Co PCS5	74
Ni PCS1	79
Ni PCS2	74
Ni PCS3	74
Ni PCS4	87
Ni PCS5	72
Cu PCS1	82
Cu PCS2	78
Cu PCS3	78
Cu PCS4	88
Cu PCS5	75

*Equimolar conc. of aldehyde, urea and ketone, ethanol as solvent, 5 mol% of M-PCS and time 8 h under reflux condition.

From the above results, we can observe that transition metals which were attached to PCS 4 show high catalytic activity. The higher conversion for the reaction done in the presence of PCS4 supported copper metal should be because of the higher surface area of the polycarbosilane support. And Cu-PCS 4 was selected as the catalyst for Biginelli reaction and further investigations were done using Cu-PCS 4 as catalyst.

4.2.1.2. Optimization of amount of Catalyst

To examine the effect of amount of catalyst in Biginelli reaction, the reaction of benzaldehyde, acetyl acetone and urea in the presence of Cu-PCS4 was stidied. The study proceeded by conducting the reaction by varying the mol % of Cu-PCS4. The reaction period was set as 8 h and the concentration of reactants as 6.5 mmol each, under reflux condition. The outcome of the study is given in table 2.

Table 2: Influence of amount of catalyst*

Entry	Mol % of catalyst	Conc. Of reactants	Conversion
1	2	6.5 mmol	65 %
2	3	6.5 mmol	76 %
3	5	6.5 mmol	88 %
4	10	6.5 mmol	92 %

*Catalyst- Cu-PCS 4, solvent-ethanol, time-8 h under reflux condition

It is observed that as the metal concentration was increased, the percentage conversion of the reaction was also increased. The amount of catalyst for the Biginelli reaction was selected as 5 mol% of Cu-PCS4.

The catalytic activity of Cu-PCS4 in Biginelli reaction with diverse sets of substrates was conducted. The products are known compounds which are identified by the comparison of spectral data from the literature.

Table 3: Biginelli reaction with different sets of substrates*

Entry	Aldehydes	β-dicarbonyls	Urea/ thiourea	Conversion (%)
1	Benzaldehyde	Acetylacetone	Urea	88
2	4-Chlorobenzaldehde	Aetylacetone	Urea	90
3	Anisaldehyde	Acetylacetone	Urea	89
4	Benzaldehyde	Ethylacetoacetate	Thiourea	75
5	Cinnamaldehyde	Acetylacetone	Urea	79
6	Anisaldehye	Ethylacetoacetate	Urea	89
7	Benzaldehyde	Ethylacetoacetate	Urea	86
8	4-Chlorobenzaldehyde	Ethylacetoacetate	Urea	90
9	Cinnamaldehyde	Ethylacetoacetate	Urea	77
10	Furfuraldehye	Ethylacetoacetate	Urea	74
11	3-Nitrobenzaldehyde	Ethylacetoacetate	Thiourea	78

*Reaction condition- equimolar conc. of aldehyde, urea and ketone, 5 mol% of Cu-PCS4 and time 8 h under reflux condition

4.2.1.3. Recycling of catalyst

The catalyst can be removed from the reaction mixture by simple filtration. It was washed thoroughly and dried. The recycled catalyst can be used for subsequent reactions without any loss of catalytic activity. The results are given in table 4.

Table 4: Catalyst recycling*

No. of cycles	Conversion (%)
1	86
2	82
3	79
4	74

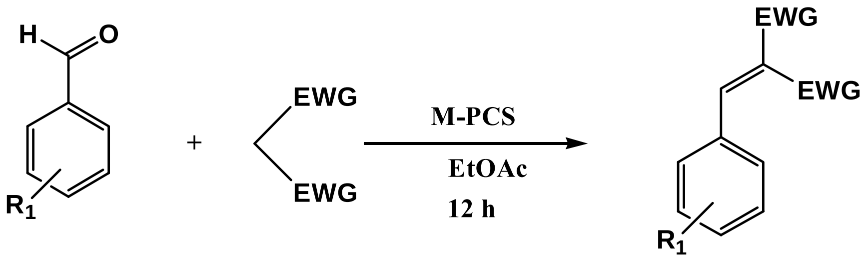
*Catalyst- 5mol% Cu-PCS 4, solvent-ethanol, time-8 h under reflux condition

It is observed that the Cu-PCS 4 retained its structure and characteristics after the completion of the reaction. Also they have all the advantages of solid phase catalysts including operational simplicity, filterability, regenerability and reuse. There was no considerable difference in the reactivity after recycling.

4.2.2. Knoevenagel Condensation Reaction

The reaction is a well known classical reaction of condensation between carbonyl compounds and compounds containing active methylene group catalysed by bases like amines[17-24]. Recently, Lewis acid catalyzed Knoevenagel reactions have also been reported[25-27]. Knoevenagel condensation is a very useful reaction and has been widely employed for carbon – carbon bond formation in organic synthesis.

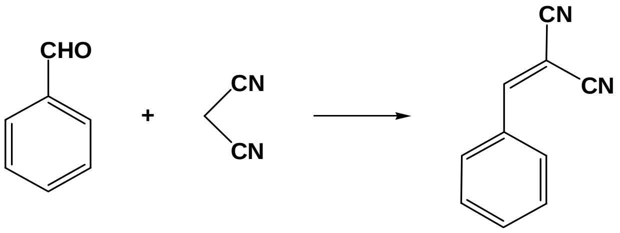
An equimolar mixture of carbonyl compound and active methylene compound with 5 mol% of catalyst was taken. The reaction mixture was stirred at room temperature for 12 h; after the work up procedure the product formed was recrystallised from ethyl acetate. The % conversion of each of the products was analyzed by HPLC with a solvent ratio, (CH_3OH:H_2O) as 70:30.



Scheme 3. Knoevenagel condensation reaction

4.2.2.1. Influence of metal attached polycarbosilanes on Knoevenagel condensation reaction

To study the effect of the nature of the support for different metal ions, the reaction was conducted with different metal ions which were attached to different polycarbosilanes. The Knoevenagel condensation reaction between benzaldehyde and malononitrile was taken in to consideration for the study; the five polycarbosilanes with metal ions such as Ti, Mn, Co, Ni and Cu were used to carry out the reaction.



Scheme 4: Knoevenagel condensation reaction with benzaldehyde and malononitrile

An equimolar mixture of benzaldehyde and malononitrile in the presence of 5 mol% metal incorporated polycarbosilane as catalyst and ethylacetate as solvent was taken. The reaction mixture was stirred at room temperature for 12 h; after the work up procedure the product formed was recrystallised from ethyl acetate. The results of the study are given in table 5.

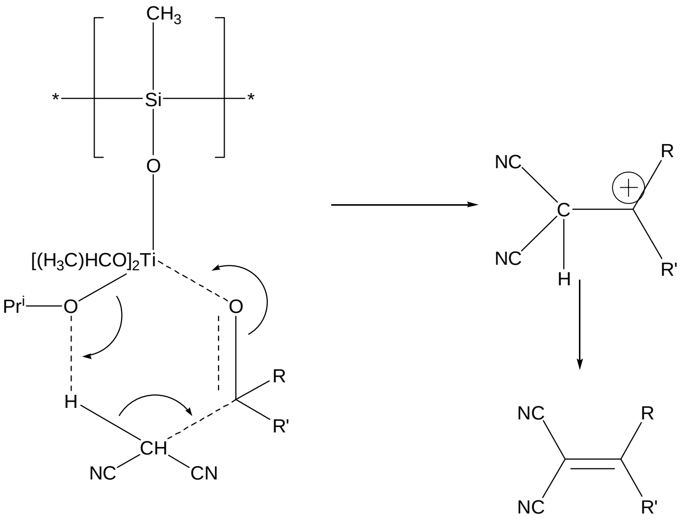
Table 5: Knoevenagel reaction with metal containing polycarbosilanes*

Catalyst	**Conversion (%)**
Ti PCS1	95
Ti PCS2	92
Ti PCS3	93
Ti PCS4	100
Ti PCS5	90
Mn PCS1	94
Mn PCS2	90
Mn PCS3	91
Mn PCS4	99
Mn PCS5	88
Co PCS1	94
Co PCS2	91
Co PCS3	90
Co PCS4	98
Co PCS5	89
Ni PCS1	94
Ni PCS2	90
Ni PCS3	89
Ni PCS4	96
Ni PCS5	87
Cu PCS1	95
Cu PCS2	92
Cu PCS3	89
Cu PCS4	97
Cu PCS5	88

*Reaction condition: 0.05mol aldehyde, 0.05mol compound with active methylene group, solvent-ethyl acetate, 5 mol% M-PCS and Time-12 h.

From the above observations, it can be concluded that transition metals which were attached to polycarbosilane with high surface area show high catalytic activity; and Ti-PCS 4 was selected as the catalyst for Knoevenagel condensation reaction and further studies were done using Ti-PCS 4 as catalyst.

The hydrophobicity of the polycarbosilane frame work plays an important role in the study (catalytic activity) since water is the by-product of the Knoevenagel condensation reaction.



Scheme 5: Possible mechanism of Ti-PCS4 catalysed Knoevenagel condensation reaction

The reaction mechanism is demonstrated in scheme 5. A six membered transition state is formed between the catalyst and the substrates. The six-membered ring rearranges and produces 2- substituted malononitrile and to regenerate the Ti-PCS4 to repeat the cycle.

4.2.2.2. Optimization of amount of catalyst

In order to quantify the catalytic performance of the titanium incorporated polycarbosilane, a model reaction between benzaldehyde and malononitrile was carried out under various reaction conditions.

Initially, the concentration of the catalyst was optimized. Equimolar concentrations of the carbonyl compound and active methylene compound were reacted in the presence of various amounts of Ti-PCS 4 in ethanol. The results are presented in table 6.

Table 6: Optimization of amount of catalyst*

Entry	Mol% of the Catalyst	Conversion (%)
1	2	85
2	3	95
3	5	100
4	10	100

*Catalyst- Ti-PCS 4, solvent-ethyl acetate, time-12 h

From the results, it is clear that the optimum amount of catalyst for the Knoevenagel condensation reaction under given conditions is 5 mol%.

4.2.2.3. Optimization of solvent for the reaction

Secondly, the role of solvent in the reaction was examined with 5mol% of Ti-PCS4. The reaction proceeded quickly in ethyl acetate, a polar solvent. In a nonpolar solvent like toluene, the reaction gave an average conversion. But reaction in water gave poor result. This phenomenon is because, the interaction between catalyst and substrate becomes difficult due to the hydrophobic nature of polycarbosilane support. In comparison with water, reaction in toluene gave good result; because the polymer will swell in toluene which makes easier interaction between the catalyst and substrate in comparison with water. The results are listed in table 7.

Table 7: Effect of solvent*

Entry	Solvent	Conversion (%)
1	Ethylacetate	100
2	Toluene	70
3	Water	40

*Catalyst- 5 mol %Ti-PCS 4, solvent-ethyl acetate, time-12 h

The generality of the catalytic activity of Ti-PCS4 was established by conducting the reaction with diverse set of substrates, which are listed in table 8. The known compounds have been identified by comparison with the previously reported spectral data (FT-IR, ^{1}H NMR and mass spectra by LC-MS) and melting point.

Table 8: Knoevenagel condensation reaction between different substrates*

Entry	Carbonyl compound	Active methylene compound	Temp. (^{o}C)	Conversion (%)
1	Benzaldehyde	Malononitrile	30	100
2	Benzaldehyde	Malonic acid	50	92
3	Anisaldehyde	Malononitrile	30	98
4	4-Chlorobenzaldehye	Malononitrile	30	100
5	4-Chlorobenzaldehye	Diethylmalonate	50	94
6	4-Hydroxybenzaldehyde	Malonic acid	50	92
7	4-Hydroxybenzaldehyde	Malononitrile	30	100
8	4-(Dimethylamino)benzaldehyde	Malononitrile	30	98
9	Benzaldehyde	Ethylcyanoacetate	50	95
10	Anisaldehyde	Ethylcyanoacetate	50	95
11	4-Chlorobenzaldehye	Ethylcyanoacetate	50	98
12	4-Hydroxybenzaldehyde	Ethylcyanoacetate	50	96
13	4-(Dimethylamino)benzaldehyde	Ethylcyanoacetate	50	92

*Reaction condition: 0.05mol aldehyde, 0.05mol compound with active methylene group, solvent-ethyl acetate, 5 mol% TiPCS4 and Time-12 h.

The metal containing polycarbosilane showed much higher activity in Knoevenagel condensation reaction compared to those performed without catalyst (no significant conversion).

4.2.2.4. Recycling of catalyst

The catalyst can be recycled by simple procedures. The catalyst removed from the reaction mixture by simple filtration was washed thoroughly and dried. The recycled catalyst can be used for subsequent reactions with out any loss of catalytic activity. The results are given in table 9.

Table 9: Recycling of the catalyst*

No. of cycles	Conversion (%)
1	100
2	98
3	93
4	91

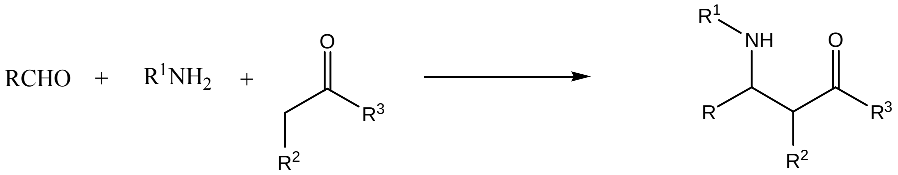
*Catalyst- 5 mol %Ti-PCS 4, solvent-ethyl acetate, time-12 h

It is observed that the Ti-PCS 4 retained its form and characteristics after the completion of the reaction. Also they have all the advantages of solid phase catalysts including operational simplicity, filterability, regenerability and reuse. There was no considerable difference in the reactivity after recycling.

4.2.3. Mannich Reaction

The Mannich type reactions are very important carbon-carbon bond forming reactions in organic synthesis and one of the most widely utilized chemical transformation for constructing β-aminoketones and other β-amino carbonyl compounds, which in turn are important synthetic intermediates for various pharmaceuticals and natural products[28-30,35]. Mannich reaction has gained popularity in synthetic chemistry over the past decades[31-36]. Most of these methods suffer from sever drawbacks including the use of large amount of catalyst, expensive reagents or catalyst, sometimes long reaction times and low conversion etc. Hence there is high interest in developing convenient methods for the synthesis of β-aminoketones. Recently, direct Mannich reactions of aldehydes, ketones and aryl amines have been achieved via Lewis acids, lanthanides, transition metal salt catalyst and organocatalytic approaches[32,33].

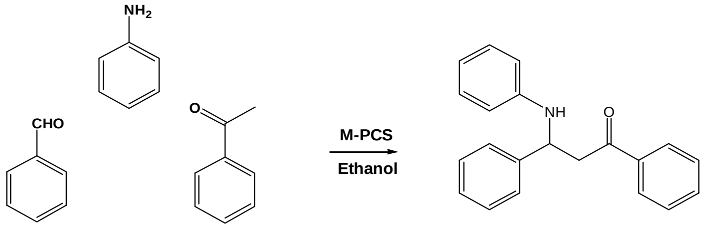
To a mixture of ketone and aldehyde, amine was added; metal incorporated polycarbosilane was added as catalyst. The reaction was conducted at room temperature.



Scheme 6: Mannich reaction

4.2.3.1. Effect of metal incorporated polycarbosilane on Mannich reaction

Inorder to study the effect of the nature of polycarbosilanes which were used as the solid support for metal ions, the reaction was conducted with different metal ions which were attached to polycarbosilanes. The reaction between benzaldehyde, aniline and acetophenone were taken as the test reaction and all the five prepared polycarbosilanes and metal ions as Ti, Mn, Co, Ni and Cu were subjected to analysis.



Scheme 7: Mannich reaction between benzaldehyde, aniline and acetophenone

An equimolar mixture of benzaldehyde, aniline and acetophenone with 5 mol% of metal incorporated polycarbosilane as catalyst was taken. Ethanol was used as the solvent. The reaction mixture was stirred at room temperature for 8 h; filtered and the product formed was recrystallised from acetone. It was then analysed by HPLC with a solvent ratio (CH_3OH:H_2O) of 75:25. The crude product was purified by column chromatography (EtOAc:Hexane). The results are as given in table 10.

Table 10: Mannich reaction catalysed by metal containing polycarbosilanes*

Catalyst	**Conversion (%)**
Ti PCS1	70
Ti PCS2	69
Ti PCS3	66
Ti PCS4	73
Ti PCS5	64
Mn PCS1	72
Mn PCS2	69
Mn PCS3	68
Mn PCS4	75
Mn PCS5	65
Co PCS1	71
Co PCS2	67
Co PCS3	68
Co PCS4	73
Co PCS5	65
Ni PCS1	71
Ni PCS2	69
Ni PCS3	67
Ni PCS4	73
Ni PCS5	62
Cu PCS1	69
Cu PCS2	67
Cu PCS3	64
Cu PCS4	74
Cu PCS5	62

*Reaction condition- equimolar conc. of aldehyde, amine and ketone, solvent-ethanol, 5 mol% of M-PCS and time 8 h.

From the above results we were able to reach on a coclusion on the catalytic activity of the metal immobilized polycarbosilane in Mannich reaction.

The metal ion which was attached to PCS4, polycarbosilane with high surface area, showed high catalytic activity. We have selected Mn-PCS 4 as the catalyst for Mannich reaction and further investigations where done using Mn-PCS 4 as catalyst.

4.2.3.2. Optimization of amount of Catalyst

To examine the effect of catalyst concentration, the reaction between benzaldehyde, aniline and acetophenone in the presence of Mn-PCS4 were considered. The study proceeded by conducting the reaction by varying the concentration of Mn-PCS4. The reaction period was set as 8 h and with equal concentrations of reactants. The outcome of the study is given in table 11.

Table 11: Optimization of the amount of catalyst*

Entry	Mol% of the Catalyst	Conversion (%)
1	2	65
2	5	75
3	10	81

*Catalyst- Mn-PCS4, solvent-ethanol and time 8 h.

It is observed that as the metal concentration increased the rate of the reaction also increased. From the results we optimised the amount of catalyst for the Mannich reaction was selected as 10 mol% of Mn-PCS4 with respect to the substrates.

The catalytic activity of Mn-PCS4, can be generalized comprehensively, by conducting the Mannich reaction with a diverse set of substrates. The crude product was purified by column chromatography (EtOAc:Hexane). All the products were characterized by FT-IR,^{1}H NMR spectroscopy, LCMS and melting point determinations. The details are listed in table 12.

Table 12: Mannich reaction with diverse sets of substrates*

Entry	Aldehydes	Amine	Ketone	Conversion (%)
1	Benzaldehyde	Aniline	Acetophenone	81
2	Anisaldehyde	Aniline	Cyclohexanone	76
3	4-Chlorobenzaldehyde	p-nitroaniline	Cyclohexanone	81
4	Anisaldehyde	p-nitroaniline	Cyclohexanone	70
5	Formaldehyde	p-nitroaniline	Cyclohexanone	70
6	4-Chlorobenzaldehyde	Aniline	Acetophenone	85
7	Naphthaldehyde	Aniline	Acetophenone	60
8	Anisaldehyde	Aniline	Acetophenone	80
9	4-Chlorobenzaldehyde	Aniline	Cyclohexanone	79
10	Benzaldehyde	Aniline	Cyclohexanone	72

*Reaction condition- equimolar conc. of aldehyde, amine and ketone, solvent-ethanol, 10 mol% of Mn-PCS4 and time 8 h.

The results indicate, the Mn-PCS 4 is acting as a good catalyst for Mannich reaction and good to high conversion were observed with all sets of substrates.

4.2.3.3. Recycling of catalyst

The catalyst can be removed from the reaction mixture by simple filtration. It was washed thoroughly and dried. The reuse of Mn-PCS4 as a catalyst for Mannich reaction was studied by conducting reaction with benzaldehyde, aniline and acetophenone in the presence of recycled Mn-PCS 4 for four cycles. The results are given in table 13.

Table 13: Recycling of catalyst*

No. of cycles	Conversion (%)
1	81
2	78
3	73
4	72

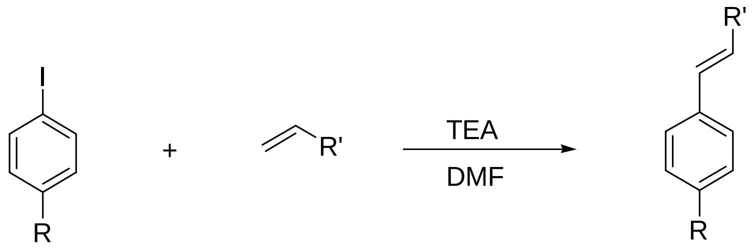
*Catalyst- 10 mol% Mn-PCS4, solvent-ethanol and time 8 h.

From the results it is clear that the recycled catalyst can be used for subsequent reactions without much loss of catalytic activity. Mn-PCS 4 has retained its form and characteristics after the completion of the reaction Also they have all the advantages of solid phase catalysts as operational simplicity, filterability, ability to regenerate and reuse. There was no considerable loss in the activity after recycling.

4.2.4. Heck Reaction

Palladium catalysis has achieved the status of an indispensable tool for both common and state-of-the art organic synthesis. Among basic types of palladium catalysed transformations, the Heck reaction and related chemistry occupy a special space. Heck reaction is the catalytic arylation and alkenylation of the olefins[37-41]. The reaction presents one of the simplest ways to obtain variously substituted olefins, dienes, and other unsaturated compounds.

Aryl, benzyl, and styryl halides react with olefinic compounds in the presence of hindered amines and a catalytic amount of palladium metal to form vinylic derivatives in which the aryl, benzyl, or styryl group has replaced a vinylic hydrogen of the original olefin. Schematic representation of heck reaction is given below.



Scheme 8: Heck reaction

To study the effect of metal ions attached to PCS4, which is the polycarbosilane with high surface area, Heck reaction was conducted in presence of copper and pallaidum ions which were attached to PCS 4. The reaction between 1-iodo-4-nitrobenzene and acrylonitrile was taken as the trial reaction to study the catalytic activity of the metal ion incorporated polycarbosilanes. The product was analysed with HPLC (Column:C18) in Solvent ratio (CH_3OH:H_2O) of 75:25. The outcome of the reaction is listed in table 14.

Table 14: Heck reaction catalysed by metal containing PCS4*

Catalyst	Conversion (%)
Cu PCS4	40
Pd PCS4	93

*Catalyst- 5 mol% M-PCS4 and time 8 h.

From the results it is clear that palladium ion attached polycarbosilane shows high catalytic activity than copper ion attached polycarbosilane.

4.2.4.1. Optimization of Amount of Catalyst

To examine the effect of catalyst concentration, the reaction of 1-iodo-4-nitrobenzene and acrylonitrile in the presence of Pd-PCS4 was analysed. The study proceeded by conducting the reaction in different amounts of Pd-PCS4. The results of the study are given in table 15.

Table 15: Optimization of amount of the catalyst*

Entry	Mol% of the Catalyst	Conversion (%)
1	2	83
2	3	92
3	5	93
4	10	98

*Catalyst- Pd-PCS4 and time 8 h.

It is observed that as the metal concentration was increased the rate of the reaction was also increased. From the results obtained and by considering the expense of palladium salts, the optimum concentration of catalyst was selected as 3 mol% with respect to the aryl halide.

The generality of the catalytic activity of Pd-PCS4 was achieved by conducting the Heck reaction with a diverse set of substrates. The products were identified by the comparison of spectral data with the reported.

Table 16: Heck reaction with different substrates*

Entry	Organic halide	Olefinic compound	Conversion (%)
1	4- Iodotoluene	Acrylonitrile	83
2	1-Iodo-4-nitrobenzene	Acrylonitrile	92
3	4- Iodotoluene	Styrene	75
4	1-Iodo-4-nitrobenzene	Styrene	79
5	4- Iodotoluene	Methyl acrylate	77
6	1-Iodo-4-nitrobenzene	Methyl acrylate	80
7	4- Iodotoluene	Methyl methacrylate	79
8	1-Iodo-4-nitrobenzene	Methyl methacrylate	83
9	1-Iodobenzoic acid	Acrylonitrile	86
10	1-Iodobenzoic acid	Methylmethacrylate	90

*Reaction condition- equimolar conc. of aryl halide and olefinic compound in the presence of 3 mol% of Pd-PCS4 at 100°C and time 8 h.

From the result of table 16, we can recommend the Pd-PCS4 as a good catalyst for Heck reaction and it gave good to excellent conversion for all the sets of substrates under consideration.

4.2.4.2. Recycling of catalyst

The catalyst can be removed from the reaction mixture by simple filtration. It was washed thoroughly and dried. The recycled catalyst can be used for subsequent reactions without any loss of catalytic activity. The results are given in table 17.

Table 17: Recycling of catalyst*

No. of cycles	Conversion (%)
1	92
2	90
3	89
4	88

*Catalyst- 3% Pd-PCS4 and time 8 h.

It is observed that the Pd-PCS 4 retained its form and characteristics after the completion of the reaction. Also they have all the advantages of solid phase catalysts including operational simplicity, filterability, regenerability and reuse. There was no considerable difference in the reactivity after recycling.

4.3. Conclusion

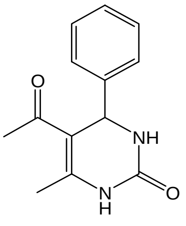
The catalytic activity of transition metal ions attached polycarbosilanes were studied. Organic reactions like Biginelli reaction, Knoevenagel condensation reaction, Mannich reaction and Heck reaction were taken into consideration for the study. Effect of PCS support on the catalytic activity was investigated. The reaction conditions were optimized and possibilities of recycling of catalysts were examined. It was observed that high surface area is a supportive aspect for the application of polycarbosilane in catalysis. The hydrophobic protection plays a major role in Knoevenagel condensation reaction.

4.4. Experimental

4.4.1. General Procedure of Biginelli reaction

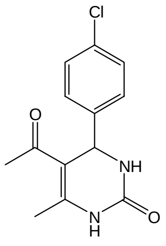
A mixture of diketone, aldehyde and urea in equal molar concentrations (8.33 mmol) were added to the copper ion incorporated polycarbosilanes (5mol %) taken in a round bottom flask. Ethanol was added as solvent. It was heated under reflux condition for 8h. The reaction mixture, after being cooled to room temperature was filtered and poured into crushed ice and stirred for 5-10 min. and recrystallised from hot ethanol to afford pure product. The products were analysed with HPLC (Column:C 18) with a solvent ratio (CH_3OH:H_2O) of 75:25. The known compounds have been identified by comparing with spectral data (FT-IR, ^{1}H NMR) and melting point with those reported. The analytical data of the compounds are presented below in the order of their entries.

Entry 1: [5 – acetyl - 3, 4–dihydro – 6– methyl–4–phenylpyrimidin–2 (1H)-one], $C_{13}H_{14}N_2O_2$



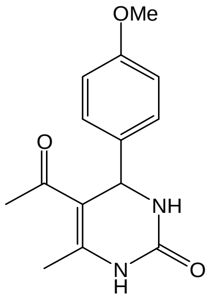
LCMS ES$^+$ (M$^+$+1) m/z: 230; **FTIR (KBr,** cm^{-1}): 3240, 2945, 670, 1601.; **^{1}H-NMR (400MHz, $CDCl_3$)**: δ 7.34-7.29 (m, 5H), 7.26 (1H, NH), 5.45 (s, 2H), 2.36 (s, 3H), 2.12 (s, 3H); **M.p.** :240°C.

Entry 2: [5-acetyl-4-(4-chlorophenyl)-3, 4-dihydro-6-methylpyrimidin-2(1H)-one], $C_{13}H_{13}ClN_2O_2$



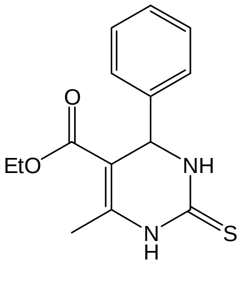
LCMS ES$^+$ (M$^+$+1) m/z: 251; **FTIR (KBr,** cm^{-1}): 3230, 1650, 1604, 1239; **^{1}H-NMR (400MHz, CDCl$_3$)**: δ 7.31-7.29 (m, 3H), 7.26-7.23 (m, 1H), 5.46 (b.s., 1H, NH), 5.45 (d, 1H), 2.35 (s, 3H), 2.16 (s, 3H); **M.p.:** 205°C.

Entry 3: [5-acetyl-3,4-dihydro-4-(4-methoxyphenyl)-6-methylpyrimidin-2(1H)-one], $C_{14}H_{16}N_2O_3$



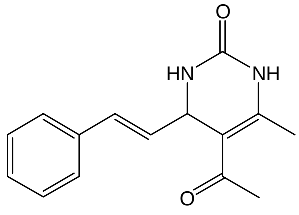
LCMS ES$^+$ (M$^+$+1) m/z: 261; **FTIR (KBr,** cm^{-1}): 3230, 2941, 1670, 1599, and 1250; **^{1}H-NMR(400MHz, CDCl$_3$)**: δ 7.22 (d, 2H), 7.12 (bs, IH, NH), 6.87 (d, 2H), 5.46 (bs, 1H, NH), 5.39 (s, 1H), 3.79 (s, 3H), 2.35 (s, 3H), 2.11 (s, 3H); **M. p.:** 182°C.

Entry 4: [Ethyl 1, 2, 3, 4-tetrahydro-6-methyl-4-phenyl-2-thioxopyrimidine-5-carboxylate], $C_{14}H_{16}N_2O_2S$



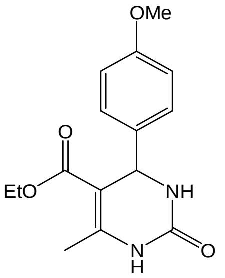
LCMS ES$^+$ (M$^+$+1) m/z: 277; **FTIR (KBr,** cm^{-1}): 3327, 2980, 1732, 1670, and 1282; **^{1}H-NMR (400MHz, CDCl$_3$)**: δ 7.76(m, 1H), 7.58(m, 1H), 7.48(m, 1H), 7.32(m, 2H), 5.41(s, 1H), 4.11(m,1H), 2.57(bs, 2H), 2.37(m, 3H), 1.17(t, 3H); **M.p.:** 205°C.

Entry 5: [5-acetyl-3,4-dihydro-6-methyl-4-styrylpyrimidin-2(1H)-one], $C_{15}H_{16}N_2O_2$



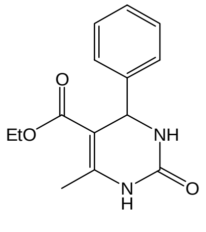
LCMS ES$^+$ (M$^+$+1) m/z: 257; **FTIR (KBr,** cm^{-1}): 3241, 2985, 1645, 1234; **^{1}H-NMR (400MHz, CDCl$_3$)**: δ 7.81 (s, 1H), 7.26-7.38 (m, 6H), 6.52 (d, 1H), 6.22 (dd, 1H), 5.70 (bs, 1H), 5.06 (d, 1H), 2.44 (s, 3H), 1.8 (s, 3H); **M.p.:** 220°C.

Entry 6: [Ethyl1,2,3,4-tetrahydro-4-(4-methoxyphenyl)-6-methyl-2-xopyrimidine-5-carboxylate], $C_{15}H_{18}N_2O_4$



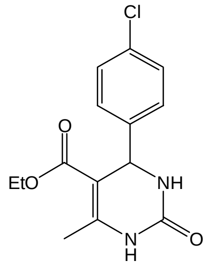
LCMS ES$^+$ (M$^+$+1) m/z: 291; **FTIR (KBr,** cm^{-1}): 3240, 2945, 1701, 1670 and 1240; **^{1}H-NMR(400MHz, CDCl$_3$)**: δ 7.26-7.22 (m, 2H), 7.02 (bs, 1H), 6.84 (d, 2H), 5.35 (s, 1H), 4.08 (q, 2H), 3.78 (s, 3H), 2.34 (s, 3H), 1.17 (t, 3H); **M.p.:** 199°C.

Entry 7: [Ethyl 1,2,3,4-tetrahydro-6-methyl-2-oxo-4-phenylpyrimidine-5-carboxylate], $C_{14}H_{16}N_2O_3$



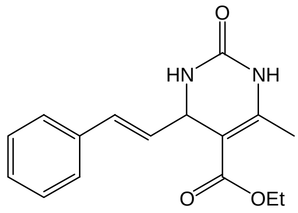
LCMS ES$^+$ (M$^+$+1) m/z: 261; **FTIR (KBr,** cm^{-1}): 3244, 2978, 1725, 1646, 1290; **^{1}H-NMR (400MHz, CDCl$_3$)**: δ 7.32-7.26 (m, 5H), 5.49 (bs, 1H), 5.40 (s, 1H), 4.10 (m, 2H), 2.35 (s, 1H), 1.16 (t, 3H); **M.p.:** 207°C.

Entry 8: [Ethyl 4-(4-chlorophenyl)-1,2,3,4-tetrahydro-6-methyl-2-oxopyrimidine-5-carboxylate], $C_{14}H_{15}ClN_2O_3$



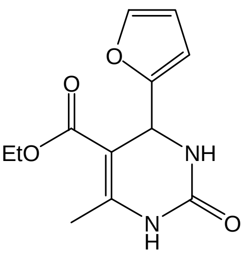
LCMS ES$^+$ (M$^+$+1) m/z: 295; **FTIR (KBr,** cm^{-1}): 3244, 1722, 1647, 1290, and 1090; **^{1}H-NMR (400MHz, $CDCl_3$)**: δ 7.68 (s, 1H), 7.20 (m, 4H), 5.60 (bs, 1H), 5.31 (d, 1H), 4.04 (m, 2H), 2.27 (s, 3H), 1.10 (t, 3H); **M.p.** :215°C.

Entry 9: [Ethyl 1,2,3,4-tetrahydro-6-methyl-2-oxo-4-styrylpyrimidine-5-carboxylate], $C_{16}H_{18}N_2O_3$



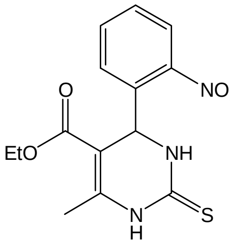
LCMS ES$^+$ (M$^+$+1) m/z: 287; **FTIR (KBr,** cm^{-1}): 3241, 2985, 1735, 1645, 1234; **^{1}H-NMR (400MHz, $CDCl_3$)** δ: 7.36-7.23 (m, 4H), 7.16 (s, 1H), 6.52 (m, 1H), 6.24 (m, 1H), 5.38 (bs, 1H), 5.02 (bm, 1H), 4.22 (m, 2H), 2.32 (s, 3H), 1.31 (t, 3H); **M.p.:** 240°C.

Entry 10: [Ethyl 4-(furan-2-yl)-1,2,3,4-tetrahydro-6-methyl-2-oxopyrimidine-5-carboxylate], $C_{12}H_{14}N_2O_4$



LCMS ES$^+$ (M$^+$+1) m/z: 252; **FTIR (KBr,** cm^{-1}): 3240, 1732, 1650 and 1290; **^{1}H-NMR (400MHz, $CDCl_3$)** δ: 8.15(m, 1H), 7.61(m, 1H), 7.51 (m, 1H), 7.47(m, 1H), 5.56(s, 1H), 3.97(m, 2H), 1.37(m, 3H), 1.10(t, 3H). **M.p.:** 203-204 °C.

Entry 11: [Ethyl 1,2,3,4-tetrahydro-6-methyl-4-(2-nitrophenyl)-2-thioxopyrimidine-5-carboxylate], $C_{14}H_{15}N_3O_4S$



LCMS ES$^+$ (M$^+$+1) m/z: 322; **FTIR (KBr,** cm^{-1}): 3434, 2981, 1715, 1531, and 853; **^{1}H-NMR (400MHz, $CDCl_3$)** δ: 8.12(m, 1H), 7.45(m, 1H), 7.30(m, 2H), 5.40(s, 1H), 4.01(m,1H), 2.53(bs, 2H), 2.35(m, 3H), 1.18(t, 3H); **M.p.:** 156-160 ^{O}C.

4.4.1.2. Optimization of amount of catalyst

To study the effect of the amount of catalyst in the reaction, Biginelli reaction of benzaldehyde, acetyl acetone and urea in the presence of Cu-PCS4 were conducted by varying the mol % of Cu-PCS4. Ethanol was used as solvent and heated to reflux. The reaction period was set as 8 h and the concentration of reactants as 6.5 mmol each.

4.4.1.3. Reuse of catalyst

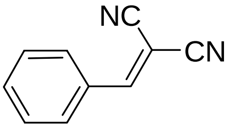
Biginelli reaction of benzaldehyde, acetyl acetone and urea, was carried out, under reflux condition in the presence of 5 mol% of Cu-PCS4 and ethanol as solvent, for 8h. After completion of the reaction the catalyst was washed thoroughly with ethyl acetate, methanol and acetone and dried under vacuum for 24 h. The recycled catalyst was then used for the reaction. The process was repeated in each cycle.

4.4.2. General procedure for Knoevenagel reaction

An equimolar mixture of carbonyl compound and active methylene compound with 5 mol% of titanium-incorporated polycarbosilane was taken with 10 mL ethylacetate in a 25 mL round bottom flask. The reaction mixture was stirred at room temperature (reaction with malononitrile was performed at

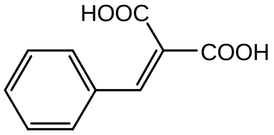
30°C, reaction with other active methylene compound was conducted at 50 °C) for 12 h and it was filtered and washed with ethyl acetate. Solvent was removed in a rotatory vacuum evaporator and washed with water. The product formed was recrystallized from ethyl acetate. All the products were analysed with HPLC (Column: C18) in a solvent ratio ($CH_3OH:H_2O$) of 70:30. The products were known compounds and were identified by comparing the spectral data (FTIR, ^{1}HNMR, and mass spectra by LCMS) and melting points with those reported. The analytical details are listed below.

Entry 1: [2-Benzylidenemalononitrile], $C_{10}H_6N_2$



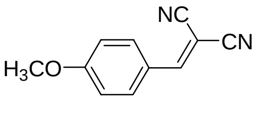
LCMS ES$^+$ (M$^+$+1) m/z: 155; **FTIR (KBr,** cm^{-1}): 2220, 1557; **H^1-NMR (400MHz, CDCl$_3$)** δ : 8.10 (m, 1H), 7.92 (m, 1H), 7.90 (m, 1H), 7.78(s, 1H), 7.54 (t, 2H); **M.p.**: 81-82°C.

Entry 2: [2- Benzylidenemalonicacid], $C_{10}H_8O_4$



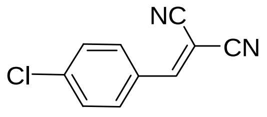
LCMS ES$^-$ (M$^+$-1) m/z: 191; **FTIR (KBr**, cm^{-1}): 3450, 2950, 1734, and 1172; **H^1-NMR (400MHz, CDCl$_3$)** δ: 10.12 (bs, 2H), 7.92 (s, 1H), 7.63 (m, 2H), 7.54 (m, 2H), 7.48 (m, 1H), 4.40 (q, 2H), 1.40 (t, 3H); **M. p.:** 103-105^{0}C.

Entry 3: [2-(4-Methoxybenzylidene)malononitrile]- $C_{11}H_8N_2O$



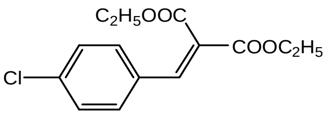
LCMS ES$^+$ (M$^+$+1) m/z: 185; **FTIR (KBr,** cm^{-1}): 2218, 1557; **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.92 (m, 2H), 7.65 (s, 1H), 7.02 (m, 2H), 3.91 (s, 3H); **M. p.:**109 - 110°C.

Entry 4: [2-(4-Chlorobenzylidene)malononitrile]- $C_{10}H_5ClN_2$



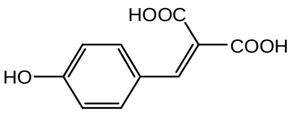
LCMS ES$^+$ (M$^+$+1) m/z: 189; **FTIR (KBr,** cm^{-1}): 2230, 1540; **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.86 (m, 2H), 7.73 (s, 1H), 7.51 (m, 2H); **M. p.**: 154 °C.

Entry 5: [Diethyl2-(4-chlorobenzylidene) malonate], $C_{14}H_{15}ClO_4$



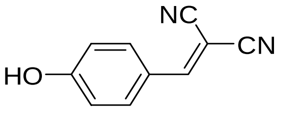
LCMS ES$^+$ (M$^+$ +1) m/z: 283; **FTIR (KBr,** cm^{-1}): 2990, 2828, 1735, 1585, and 1086; **H^1-NMR (400MHz, CDCl$_3$)** δ: 8.05 (m, 2H), 7.90 (d, 1H), 7.47 (m, 2H), 4.41 (m, 4H), 1.40 (m, 6H); **M. p.:** 208^{0}C

Entry 6: [2-(4-hydroxybenzylidene)malonicacid], $C_{10}H_8O_5$



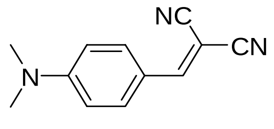
LCMS ES$^+$ (M$^+$+1) m/z: 209; **FTIR (KBr,** cm^{-1}**)**: 3394, 2952, 1673, 1515, and 1285; **H^1-NMR (400MHz, CDCl$_3$)** δ: 10.53 (bs, 2H) 7.82 (s, 1H), 7.54 (m, 2H), 6.99 (m, 2H), 1.99 (bs, 1H); **M. p.**: 115-118 °C.

Entry 7: [2-(4-Hydroxybenzylidene)malononitrile]- $C_{10}H_6N_2O$



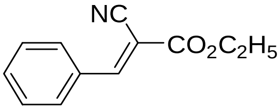
LCMS ES$^+$ (M$^+$+1) m/z: 171; **FTIR (KBr,** cm^{-1}**)**: 3450, 2358, 1416; **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.88 (m, 2H), 7.64 (s, 1H), 6.97 (m, 2H), 6.37 (bs, 1H); **M. p.**: 182 °C.

Entry 8: [2-(4-(Dimethylamino)benzylidene)malononitrile], $C_{12}H_{11}N_3$



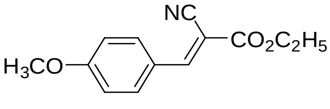
LCMS ES$^+$ (M$^+$+1) m/z: 198; **FTIR (KBr**, cm^{-1}): 2932, 2358, 1647, 1516, 1320, and 1087. **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.82 (m, 2H), 7.46 (s, 1H), 6.71 (d, 2H), 3.16 (s, 6H). **M. p**.:177-180°C.

Entry 9: [Ethyl 2-cyano-3-phenylacrylate]- $C_{12}H_{11}NO_2$



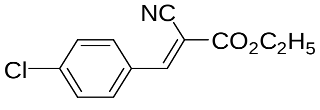
LCMS ES$^+$ (M$^+$+1) m/z: 202; **FTIR (KBr,** cm^{-1}**)**: 2932, 2358, 1747, 1416, and 1087; **H^1-NMR (400MHz, CDCl$_3$)** δ: 8.12 (m, 2H), 7.63 (m, 1H), 7.48 (m, 2H), 4.40 (q, 2H), 1.40 (t, 3H); **M. p**.: 52 °C.

Entry 10: [Ethyl 2-cyano-3-(4-methoxyphenyl)acrylate]- $C_{13}H_{13}NO_3$



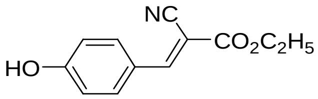
LCMS ES$^+$ (M$^+$+1) m/z: 232; **FTIR (KBr,** cm^{-1}**)**: 2982, 2358, 1704 and 1040; **H^1-NMR (400MHz, CDCl$_3$)** δ: 8.08 (m, 2H), 6.96 (m,3H), 4.08 (q, 2H), 3.41 (s, 3H), 1.17 (t, 3H); **M. p**.: 90 °C.

Entry 11: [Ethyl 3-(4-chlorophenyl)-2-cyanoacrylate]- $C_{12}H_{10}ClNO_2$



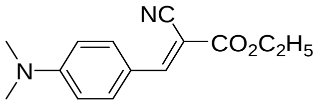
LCMS ES$^-$(M$^+$-1) m/z: 234; **FTIR (KBr,** cm^{-1}**)**: 2932, 2358, 1747, 1416, 1320; **H^1-NMR (400MHz, CDCl$_3$)** δ: 8.05 (m, 2H), 7.94 (d, 1H), 7.47 (m, 2H), 4.40 (q, 2H), 1.40 (t, 3H); **M. p.:**162-164°C.

Entry 12: [Ethyl 2-cyano-3-(4-hydroxyphenyl)acrylate]- $C_{12}H_{11}NO_3$



LCMS ES$^+$ (M$^+$+1) m/z: 218; **FTIR (KBr,** cm^{-1}**)**: 3445, 2932, 2358, 1747, and 1047; **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.82 (m, 2H), 6.99 (m, 3H), 4.42 (q, 2H), 1.89 (bs, 1H), 1.39 (t, 3H); **M. p.**: 169-170°C.

Entry 13: [Ethyl 2-cyano-3-(4-(dimethylamino)phenyl)acrylate]- $C_{14}H_{16}N_2O_2$



LCMS ES$^+$ (M$^+$+1) m/z: 245; **FTIR (KBr,** cm^{-1}**)**: 2932, 2358, 1747, 1416, 1320, and 1087; **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.75 (d, 2H), 6.7 (d, 3H), 4.34 (q, 2H), 3.1 (s, 6H), 1.37 (t, 3H); **M. p.**: 65-70°C.

4.4.2.3. Optimization of amount of catalyst

Equimolar concentrations of benzaldehyde and malononitrile were reacted in the presence of 2, 3, 5 and 10 mol% of Ti-PCS 4 in ethyl acetate at room temperature. The % conversion was observed in each case.

4.4.2.4. Optimization of solvent

The reaction between benzaldehyde and malononitrile was examined with 5 mol% of Ti-PCS4 in different solvents such as ethyl acetate, toluene and water. The % conversions were checked in each case.

4.4.2.5. Reuse of catalyst

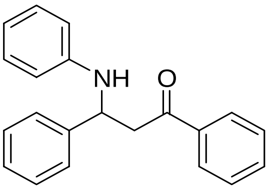
Reuse of catalyst was checked as follows: Knoevenagel condensation reaction of benzaldehyde and malononitrile was carried out under optimized reaction condition. After completion of the reaction the catalyst was removed from the reaction mixture by filtration and washed thoroughly with ethyl acetate, methanol and acetone and then dried under vacuum for 24 h. The process was repeated in each cycle.

4.4.3. General procedure for Mannich reaction

All the substrates used for the reaction were purified by standard procedures. The Mannich type reaction of aromatic aldehyde, ketone and aromatic amine led to the efficient synthesis of β-aminoketones under mild conditions.

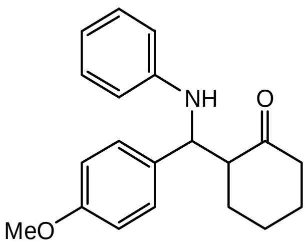
To a mixture of ketone (1eq) and aldehyde (1eq), amine (1eq) was added in a small round bottom flask fitted with a condenser. To this mixture Mn-PCS 4 (5 mol %) and ethanol (10 mL) as solvent was added and stirred at room temperature for 8 h. The progress of the reaction was monitored by thin layer chromatography (1:4 EtOAc: Hexane). After the reaction was completed, the reaction mixture was stirred with ethanol and filtered. It was evaporated in a rotatory evaporator and the precipitated solid was recrystallised using acetone. The crude product was purified with silica column chromatography (EtOAc: Hexane). The purity of the product was analyzed by reverse phase HPLC in the solvent ratio of 75:25 (methanol: water). The flow rate and temperature of HPLC were 1ml/minute and 28 ^{0}C respectively. The products were known compounds and were identified by comparison of spectral data (FTIR, ^{1}HNMR, and mass spectra by LCMS) and melting points with those reported. The spectral data of selected entries are listed below.

Entry 1: 1, 3-diphenyl-3-(phenylamino)propan-1-one, $C_{21}H_{19}NO$



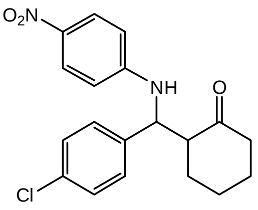
LCMS ES$^+$ (M$^+$+1) m/z: 302; **FTIR (KBr,** cm^{-1}**)**: 3442, 2923, 1665, 1597; **^{1}H NMR(400,CDCl$_3$)** δ: 7.91 (dd, 1H), 7.76-7.11 (m, 10H), 6.67 (t, 1H), 6.54 (d, 2H), 5.02 (m, 1H), 3.53 (m, 2H); **M. p.:** 154-156 °C.

Entry 2: 2-((phenylamino)(4-methoxyphenyl)methyl)cyclohexanone, $C_{20}H_{23}NO_2$



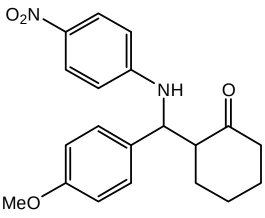
LCMS ES$^+$ (M$^+$+1) m/z: 310; **FTIR (KBr,** cm^{-1}**)**: 3435, 1662, 1595, 1085; **H^1-NMR (400MHz, CDCl$_3$)**: 7.75 (s, 1H), 7.46-7.43 (m, 4H), 6.95-6.91 (m, 4H), 3.84 (m, 4H), 2.93-2.89 (m, 3H), 2.16 (s, 2H), 1.81-1.78 (m, 2H), 1.60 (s, 2H); **M. p.**: 158 °C.

Entry 3: 2-((4-nitrophenylamino)(4-chlorophenyl)methyl)cyclohexanone, $C_{19}H_{19}ClN_2O_3$



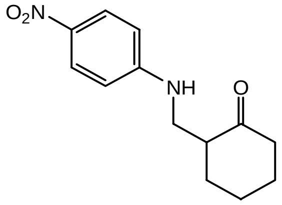
LCMS ES$^+$ (M$^+$+1) m/z: 359; **FTIR (KBr,** cm^{-1}**)**: 3423, 1658, 1590, 1080; **H^1-NMR (400MHz, CDCl$_3$)**: 7.72 (s, 2H), 7.40-7.38 (m, 4H), 7.26 (s, 2H), 3.95 (m, 1H), 2.91-2.87 (m, 3H), 2.16 (s, 2H), 1.82-1.79 (m, 2H), 1.56 (s, 2H); **M. p.**: 140°C.

Entry 4: 2-((4-nitrophenylamino)(4-methoxyphenyl)methyl)cyclohexanone, $C_{20}H_{22}N_2O_4$



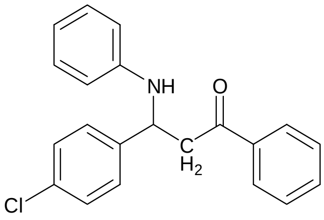
LCMS ES$^+$ (M$^+$+1) m/z: 355; **FTIR (KBr,** cm^{-1}**)**: 3420, 1645, 1589, 1079; **H^1-NMR (400MHz, CDCl$_3$)**: 7.75 (s, 2H), 7.46-7.43 (m, 4H), 6.94-6.92 (m, 2H), 3.84 (m, 4H), 2.93-2.89 (m, 3H), 2.16 (s, 2H), 1.81-1.80 (m, 2H), 1.61 (s, 2H); **M. p.**: 158°C.

Entry 5: 2-((4-nitrophenylamino)methyl)cyclohexanone, $C_{13}H_{16}N_2O_3$



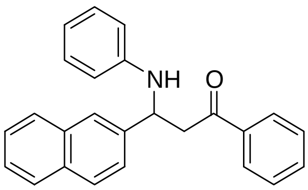
LCMS ES$^+$ (M$^+$+1) m/z: 249; **FTIR (KBr,** cm^{-1}): 3425, 1647, 1595, 1080; H^1-NMR (300MHz, $CDCl_3$): 7.73(m, 2H), 7.35(m, 1H), 7.18(s, 1H), 2.88(m, 1H), 2.09(s, 1H), 1.72(m, 6H), 1.52(bs, 1H), 1.18(m, 2H); **M. p.**: 114°C.

Entry6: 3-(4-chlorophenyl)-1-phenyl-3-(phenylamino)propan-1-one, $C_{21}H_{18}ClNO$



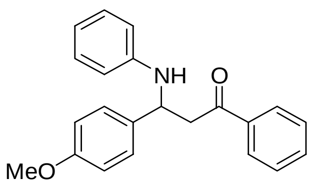
LCMS ES$^+$ (M$^+$+1) m/z: 336; **FTIR (KBr,** cm^{-1}): 3434, 2626, 1654, 1594 and 1080; **^{1}H NMR(400,$CDCl_3$)** δ: 3.38-3.51(m,2H) ,4.56(s,1H), 4.96-4.99(m,1H), 6.52-6.54(m,2H), 6.69-6.66(t,1H,J=7.2Hz), 7.07-7.11(m,2H), 7.27-7.29(m,1H), 7.37(m,1H), 7.39(m,2H), 7.43-7.47(m,2H), 7.56-7.57(m,1H), 7.88-7.91(m,2H). **M. p.:** 110-112 °C.

Entry 7: 3-(naphthalen-3-yl)-1-phenyl-3-(phenylamino)propan-1-one, $C_{25}H_{21}NO$



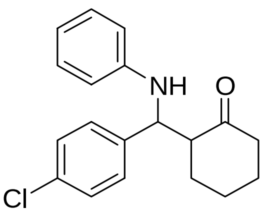
LCMS ES$^+$ (M$^+$+1) m/z: 352; **FTIR (KBr,** cm^{-1}): 3444, 2921, 1656, 1611. **^{1}H NMR(400,$CDCl_3$)** δ: 8.67 (m, 2H), 8.29-7.52 (m, 13H), 6.84 (m, 2H), 4.89 (s, 1H), 3.88 (m, 2H); **M. p.:** 120-122°C.

Entry 8: 3-(4-methoxyphenyl)-1-phenyl-3-(phenylamino)propan-1-one, $C_{22}H_{21}NO_2$



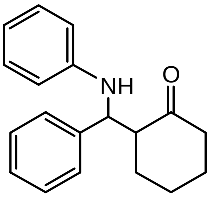
LCMS ES$^+$ (M$^+$+1) m/z: 332; **FTIR (KBr,** cm^{-1}**)**: 3442, 2921, 1647, 1532, 1021; **^{1}H NMR(400,CDCl$_3$)** δ: 7.91 (dd, 2H), 7.57 (m, 1H), 7.46 (m, 2H), 7.36 (m, 2H), 7.10 (m, 2H), 6.86 (m, 2H), 6.65 (t, 1H), 6.57 (d, 1H), 4.97 (m, 1H), 4.50 (bs, 1H), 3.76 (s, 3H), 3.50-3.37 (m, 2H); **M. p.:** 104-106°C.

Entry 9: 2-((phenylamino)(4-chlorophenyl)methyl)cyclohexanone, $C_{19}H_{20}ClNO$



LCMS ES$^+$ (M$^+$+1) m/z: 314; **FTIR (KBr,** cm^{-1}**)**: 3423, 1658, 1590, 1081; **^{1}H NMR(400,CDCl$_3$)** δ: 7.43-7.42 (m, 4H), 7.35-7.34 (m, 2H), 7.33-7.30 (m, 4H), 4.56 (m, 1H), 2.82 (t, 1H), 2.81 (m, 2H), 2.80-2.78 (m, 4H), 2.55-2.52 (m, 2H):**M. p.:** 134-136 °C.

Entry 10: 2-((phenylamino)(phenyl)methyl)cyclohexanone, $C_{19}H_{21}NO$



LCMS ES$^+$ (M$^+$+1) m/z: 280; **FTIR (KBr,** cm^{-1}**)**: 3433, 1660, 1598 and 1087; **H^1-NMR (400MHz, CDCl$_3$)**: 7.50 (t, 2H), 7.37 (m, 5H), 7.34-7.26(m, 3H), 4.26 (s, 1H), 2.8 (m, 1H), 2.5 (t, 2H), 1.95(m, 2H), 1.78-1.57(m, 2H), 1.25(s, 2H), 0.88(bs, 1H); Yellow oily product.

4.4.3.1. Optimization of amount of catalyst

Mannich reaction of benzaldehyde, acetyl acetone and urea in the presence of Mn-PCS4 was analysed. The study proceeds by conducting the reaction by varying the concentration of Mn-PCS4 by 2, 5, 10 mol%. The reaction period was set as 8 h and with equal concentrations of reactants.

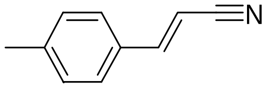
4.4.3.2. Recycling of catalyst

The catalyst can be removed from the reaction mixture by simple filtration. It was washed thoroughly with methanol, water and acetone and dried. The recycled Mn-PCS4 was used as a catalyst for Mannich reaction of benzaldehyde, aniline and acetophenone. The whole process was repeated for four cycles

4.4.4. General procedure for Heck reaction

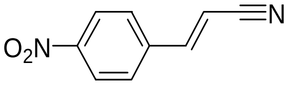
To a round bottom flask containing 3 mol% of palladium containing PCS4, equal concentrations of organic halide (20 mmol), olefinic compound (20 mmol) and 20 mmol of triethyl amine were added. DMF was used as the solvent. A water cooled condenser was placed on the flask and stirred for about 12 h at 100^{o}C. The reaction mixture was filtered and washed with dichloromethane and then with water. The filtrate was extracted with diethyl ether. The ether layer was collected and dried over anhydrous sodium sulphate. It was then filtered and solvents were removed in a rotator evaporator. The residue was recrystallised from dichloromethane. The products were analysed with HPLC (Column:C18) in a Solvent ratio (CH_3OH:H_2O) of 75:25. The products were known compounds and were identified by comparison of spectral data (FTIR, ^{1}HNMR, and mass spectra by LCMS) and melting points with those reported. The spectral data of selected entries are listed below.

Entry 1: (*E*)-3-p-tolylacrylonitrile, $C_{10}H_9N$



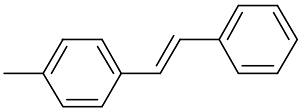
LCMS ES$^+$ (M$^+$-1) m/z: 142; **FTIR (KBr,** cm^{-1}**)**: 3037, 2932, 2258, 1587, 1320, and 977; **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.39, 7.34 (d, 1H, J= 16Hz), 7.55,7.35(d, 1H), 7.22, 7.20(d, 1H), 5.84, 5.80(d, 1H, J=16Hz), 2.38(s, 3H); **M. p.:** 48 °C.

Entry 2: (*E*)-3-(4-nitrophenyl)acrylonitrile, $C_9H_6N_2O_2$



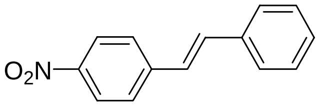
LCMS ES$^+$ (M$^+$+1) m/z: 175; **FTIR (KBr,** cm^{-1}**)**: 3066, 2927, 2213, 1596, 1341, 968; **H^1-NMR (400MHz, CDCl$_3$)** δ: 8.32-8.27(m, 1H), 7.97(d,1H), 7.8(d,1H), 7.64, 7.62(d, 1H, J=16Hz), 6.07, 6.03(d, 1H, J=16Hz); **M. p.:**203- 204 °C.

Entry 3: (*E*)-1-methyl-4-styrylbenzene, $C_{15}H_{14}$



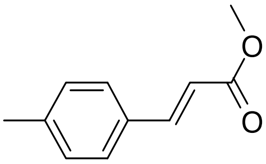
LCMS ES$^+$ (M$^+$+1) m/z: 195; **FTIR (KBr,** cm^{-1}**)**: 3018, 2921, 1591, 968; **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.51-7.49 (m, 2H), 7.42-7.40 (d, 2H), 7.36-7.33 (m, 2H), 7.24 (m, 1H), 7.17 (m, 2H), 7.07 (d, 2H), 2.36 (s, 3H); **M. p.:** 117-118 °C.

Entry 4: (*E*)-1-(4-nitrostyryl)benzene, $C_{14}H_{11}NO_2$



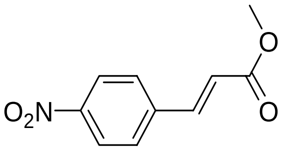
LCMS ES$^+$ (M$^+$+1) m/z: 226; **FTIR (KBr,** cm^{-1}**)**: 3088, 2822, 1585, 1340, 965; **H^1-NMR (400MHz, CDCl$_3$)** δ: **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.98-7.97 (m, 2H), 7.65-7.63 (d, 2H), 7.36-7.33 (m, 2H), 7.24 (m, 1H), 7.17 (m, 2H), 7.06 (d, 1H); **M. p.:** 153-155 °C.

Entry 5: (*E*)-Methyl 3-p-tolylacrylate, $C_{11}H_{12}O_2$



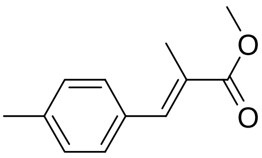
LCMS ES$^+$ (M$^+$+1) m/z: 177; **FTIR (KBr,** cm^{-1}**)**: 3055, 2930, 1747, 1346 and 987; **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.69, 7.65 (d, 1H, J=16Hz), 7.43 (d, 2H), 7.20 (d, 2H), 6.41, 6.37 (d, 2H, J=16Hz), 3,80 (s, 3H), 2.37 (s, 3H); Pale yellow oil.

Entry 6: (*E*)-Methyl 3-(4-nitrophenyl)acrylate, $C_{10}H_9NO_4$



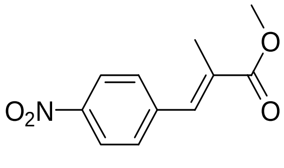
LCMS ES$^+$ (M$^+$+1) m/z: 208; **FTIR (KBr,** cm^{-1}**)**: 3037, 2927, 1725, 1342 and 995; **H^1-NMR (400MHz, CDCl$_3$)** δ: 8.26 (dt, 2H), 7.74, 7.70 (d, 1H, J=16Hz), 7.67 (dt, 2H), 6.58, 6.54 (d, 1H, J=16 Hz), 3.84 (s, 3H); **M. p.:** 158-160 °C.

Entry 7: (*E*)-Methyl 2-methyl-3-p-tolylacrylate, $C_{12}H_{14}O_2$



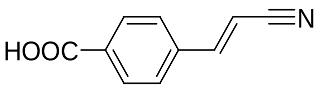
LCMS ES$^+$ (M$^+$+1) m/z: 191; **FTIR (KBr,** cm^{-1}**)**: 3087, 2932, 1747, 1320, and 967; **H^1-NMR (400MHz, CDCl$_3$)** δ: 8.15(m, 1H), 7.89(d,1H), 7.76(m, 1H), 7.74(d,1H), 7.25, 7.21(d, 1H, J=16Hz), 3.54(m, 3H), 2.51(s, 1H) 1.94(m, 3H) . Oily in nature.

Entry 8: (*E*)-Methyl 2-methyl-3-(4-nitrophenyl)acrylate, $C_{11}H_{11}NO_4$



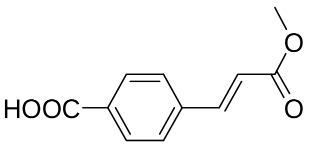
LCMS ES$^+$ (M$^+$+1) m/z: 222; **FTIR (KBr,** cm^{-1}**)**: 3087, 2930, 1707, 1340 and 927; **H^1-NMR (400MHz, CDCl$_3$)** δ: **H^1-NMR (400MHz, CDCl$_3$)** δ: 8.16(m, 1H), 7.82(d,1H), 7.66(m, 1H), 7.71(d,1H), 7.26, 7.22(d, 1H, J=16Hz), 3.55(m, 3H), 2.01(m, 3H) . **M. p.:** 235 °C.

Entry 9: 4-((E)-2-cyanovinyl)benzoic acid, $C_{10}H_7NO_2$



LCMS ES$^+$ (M$^+$+1) m/z: 174; **FTIR (KBr,** cm^{-1}**)**: 3540, 3066, 2213, 1680, 1596, 1281, 968; **H^1-NMR (400MHz, CDCl$_3$)** δ: **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.99 (bs, 1H), 7.73 (m, 2H), 7.65 (m, 2H), 7.38, 7.34 (d, 1H, J= 16Hz), 5.85, 5.81(d, 1H, J=16Hz); **M. p.:** 178 °C

Entry 10: 4-((E)-2-(methoxycarbonyl)vinyl)benzoic acid, $C_{11}H_{10}O_4$



LCMS ES$^+$ (M$^+$+1) m/z: 207.16; **FTIR (KBr,** cm^{-1}**)**: 3540, 3086, 2930, 1707, 1680, 1596, 1281 and 927; **H^1-NMR (400MHz, CDCl$_3$)** δ: **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.98 (bs, 1H), 7.71 (t, 1H), 7.70 (t, 2H), 7.66 (t, 2H), 7.74 (t, 1H), 3.10 (m, 3H); **M. p.:** 174 °C

4.4.4.1. Optimization of amount of catalyst

To optimize the catalyst concentration, the reaction of 1-iodo-4-nitrobenzene and acrylonitrile in the presence of Pd-PCS4 by varying the concentration as 2, 3, 5, 10 mol%. The % conversion was analysed in each case.

4.4.4.2. Recycling of catalyst

The catalyst can be removed from the reaction mixture by simple filtration. It was washed thoroughly with methanol, chloroform and acetone and dried. The heck reaction of 1-iodo-4-nitrobenzene and acrylonitrile in the presence of 3 mol% of Pd-PCS4 was conducted. The reaction was repeated for four cycles.

4.5. References

1. Mukaerjee, S.; Yang, J. W.; Hoffmann, S.; List, B. *Chem. Rev.* **2007**, *107*, 5471.
2. Wan, Y.; Wang, H.; Zhao, Q. Klingstedt, M.; Terasaki, O.; Zhao, D. *J. Am. Chem. Soc.* **2009**, *131*, 4541.
3. Ma, X.; Zhou, Y.; Zhang, J.; Zhu, A.; Jiang, T.; Han, B. G*reen Chem.* **2008,** *10*, 59.
4. Bose, D. S.; Fatima, L.; Mereyala, H. B. *J. Org. Chem.* **2003**, *68*, 587.
5. Li, C. J. *Chem. Rev.* **2005**, *105*, 3095.
6. Jain, S. L.; Joseph, J. K.; Singhal, S.; Sain, B. *J. Mol. Catal. A: Chemical* **2006**, *268*, 134.
7. Furstner, A.; Leitner, A.; Mendez, M.; Krause, H. *J. Am. Chem. Soc.* **2002**, *124*, 13856.
8. Velusamy, S.; Punniyamurthy, T. *Org.Lett.* **2004,** *6*, 217.
9. Kazmierski, I.; Bastienne, M.; Gosmini, C.; Paris, J. M.; Perichon, J. *J. Org. Chem.* **2004,** *69*, 936.
10. Durandetti, M.; Nedelec, J. Y.; Perichon, J. *Org.Lett.* **2001**, *3*, 2073.
11. Dvornic, P. R.; Owen, M. J. *Silicon-Containing Dendritic Polymers Advances in Silicon Science,* **2009**, 2, USA, Springer
12. Song, Y. C.; Hasagawa, Y.; Yang, S. J.; Sato, M. *J. Mater. Sci.* **1988**, *23*, 1911.
13. Chen, X. H.; Xu, X. Y.; Liu, H.; Cun, L. F.; Gong, L. Z. *J. Am. Chem. Soc* **2006**, *128*, 14803.
14. Nilson, B. L.; Overman, L. E. *J. Org. Chem.*, **2006**, *71*, 7706

15. Gross, G. A.; Wurziger, H.; Schober, A. *J. Comb. Chem.* **2006,** *8*, 153.
16. Kappe, C. O. *Acc.Chem. Res.*, **2000,** *33*, 879.
17. Ware, M.; Madje, B.; Pokalwar, R.; Kakade, G.; Shingare, M. *Bulletin of the Catalysis Society of India,* 2007, *6*, 104.
18. Yue, C.; Mao, A.; Wei, Y.; Lu, M. *Catal.Commun,* **2008**, *9*, 1571.
19. Reddy, K. R.; Rajgopal, K.; Maheswari, C. U.; Kantam, M. L. *New J. Chem*. **2006**, *30*, 1549.
20. Krishnan, G. R.; Thomas, J.; Sreekumar, K. *ARKIVOC*, **2009**, *x*, 106-120.
21. Yamashita, K.; Tanaka, T.; Hayashi, M.; *Tetrahedron* **2005,** *61*, 7981.
22. Goa, Y.; Wu, P.; Tatsumi, T.; *J. Catal*. **2004**, *224*, 107.
23. Hassan, V.; Hamid, G. *Synthetic Commun.* **2010**, *40*, 1477.
24. Georgeta, P.; Biswajit, C.; Bikash, K.; Kumari, P.; Julie, B.; Aline, A. *J. Catal.* **2010**, *269*, 110.
25. Prajapati, D.; Sandhu, J. S. *J. Chem. Soc. Perkin Trans. 1*, **1993**, 739.
26. Liao, J.; Wang, Q. *Macromolecules* **2004,** *37*, 7061.
27. Evdokimov, N. M.; Kireev,A. S.; Yakovenko, A. A.; Yu, M.; Magedov, A. I.; Kornienko, A. *J. Org. Chem.* **2007**, *72*, 3443.
28. Josephsohn, N. S.; Snapper. M. L.;Hoveyda,A. H. *J. Am. Chem. Soc.* **2004**, *126*, 3734.
29. Song, J.; Wang, Y.; Deng, L. *J. Am. Chem. Soc.* **2006**, *128*, 6048.
30. Wenzel, N. I.; Chavain, N.; Wang, Y.; Friebolin, W.; Maes, L.; Pradines, B.; Lanzer, M.; Yardly, V.; Brun, R.; Herold-mende, C.; Biot, C.; Toth, K; Davioud-Charvet, E. *J. Med.Chem.* **2010**, *53*, 3214.

31. Youngman, M. A.; Dax, S. L. *J. Comb.Chem.*, **2001**, *3*, 469.
32. Wang, R.; Li, B. G.; Huang, T. K.; Shi, L.; Lu, X. X. *Tetrahedron Letters* **2007**, *48*, 2071.
33. Loh, T. P.; Chen, S. L. *Org.Lett.* **2002**, *4*, 3647.
34. Manabe, K.; Kobayashi, S. *Org. Lett.* **1999**, *1*, 1965.
35. List, B. *J. Am. Chem. Soc.* **2000**, *122*, 9336.
36. Pacorel, B.; Leung, S. C.; Stachulski, A. V.; Davies, J.; Vivas, L.; Lander, H.; Wars, S. A.; Kaiser, M.; Brun, R.; Ó Neill, P. M. *J. Med.Chem*. **2010**, *53,* 633.
37. Bräse, S.; Kirchoff, J. H.; Köbberling, J.; *Tetrahedron*, **2003**, *59*, 885.
38. Dieck, H. A.; Heck, R. F. *J. Org. Chem.,* **1975**, *40*, 1083.
39. Heck, R. F. *J. Am. Chem. Soc.,* **1968,** *90*, 5518.
40. Heck, R. F. *Acc. Chem. Resear.* **1979**, *12*, 146.
41. Beletskaya, I. P.; Cheprakov, A. V. *Chem. Rev.*, **2000**, *100*, 3009.

Chapter 5

SYNTHESIS OF FUNCTIONALISED POLYSILANE: APPLICATION AS ORGANOCATALYSTS

Contents

5.1. Introduction

Dendrimers are monodispersed large molecules composed of two or more tree like dendrons. They are highly branched macromolecules[1-3], obtained by a sequence of reaction steps and are characterized by their structure perfection. A dendrimer is usually symmetric around the core and often accept a spherical three dimensional morphology. The different properties of large dendrimers compared to their conventional polymeric counter parts make these molecules interesting compounds for material science. Dendrimers are mainly used in the area of catalysis and in biotechnology and for medicinal applications[4-6].

Solid phase syntheses of dendrimers[7,8] are really a challenge because of the large number of reactions that take place simultaneously during the building up of each generation and the number increases exponentially with increase in generation. Conversely, solid phase synthesis provides some inherent advantages over solution phase synthesis. Synthesis of dendrimers needs large excess of reagents for obtaining high purity and defect free products. Solid phase synthesis usually uses large excess of reagents, but purification of intermediates is easy which is the most tedious step in solution phase synthesis. The polymer on which the dendrimer is synthesized can be used as high load resin for combinatorial synthesis; and also can find application in heterogeneous catalysis. These materials can also be used in bioassays in which the polymer supported dendrimer with suitable surface groups act as multivalent ligands for various biological receptors.

In the synthesis of dendrimer, two strategies were generally employed and they are divergent synthesis and convergent synthesis. In divergent method, the synthesis starts from a core and extended outward by a series of reactions. In convergent method[9], small dendrons are prepared and they are attached to a core molecule. Divergent synthesis is more suitable and widely employed for solid phase synthesis of dendrimer.

Dendrimers are considered to fill the gap between homogeneous and heterogeneous catalysis. The dendrimer functionalized polymers can be used as heterogeneous catalyst.

Dendrimer can combine the advantages of both homogeneous and heterogeneous catalytic systems[1-3]. They show the activity and selectivity of a conventional homogeneous catalyst, while they can be recovered from the reaction medium easily. The interior regions of a dendrimer can provide a localised environment suitable for binding and catalysis. For example, it has been demonstrated that water-soluble dendrimers can ‘dissolve’ small hydrophobic molecules with in them in much the same way that a micelle can. This provides a mechanism for the concentration of reactive species with in a small localized and controlled microenvironment (any increase in concentration will be accompanied by an increase in the rate of reaction). It can therefore be envisaged that many traditional organic reactions could be catalysed in bulk aqueous solution.

Several scientific groups[10,11] have utilized the highly branched nature of dendrimeric materials to obtain multivalent ligands for the use in catalysis. There are many examples for the use of peripherally functionalised dendrimers in homogeneous catalysis. However, little attention has been paid to the use of dendrimers in heterogeneous catalysis. Most dendrimer catalysts are functionalised at the periphery with catalytic groups; however, core and inner branch functionalized solid supported dendrimer catalysts have also been developed. Dendrimer supported catalysts have the added advantage that the active catalyst and dendrimer are solvated, making the catalytic sites more available in solution (relative to polymers). Insoluble supported dendrimers are easy to be removed from solutions as precipitates *via* filtration.

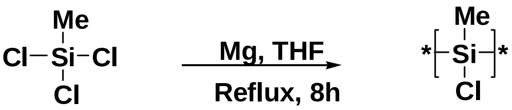
PPI-dendrimers stands for “poly (propylene imine)” describing propyl amine spacer moities in the oldest known dendrimer type developed initially by Vögtle[12]. These dendrimers are generally polyalkylamines having primary amines as end-groups; the dendrimer interior consists of numerous tertiary trispropylene amines. PPI-dendrimers were prepared on heterogeneous support via a divergent approach that was based on a repeated double alkylation of amines with acrylonitrile by “Michael addition” resulting in a branched alkyl chain structure[13]. Subsequent reduction yielded a new set of primary amines, which might then be double alkylated to provide further branching.

The present chapter deals with the discussion about polysilane supported dendrimers and their application. Polysilane was synthesized from the monomer, trichloromethylsilane. The polysilane supported PPI dendrimer was prepared by divergent method and dendrimer upto the third generation was prepared. Successive Michael addition and reduction were used to synthesize PPI dendrimer. The polysilane functionalized with dendrimer was characterized by FT-IR, ^{29}Si-CP-MAS NMR, ^{13}C NMR spectroscopy and amino group estimations. The catalytic activity of PPI dendrimer immobilized polysilane was studied. Knoevenagel condensation reaction was selected to study the catalytic activity. Reaction conditions were optimized.

5.2. Results and discussion

5.2.1. Preparation of polysilane

Silicon polymers resulting from monomers by Wurtz type coupling were insoluble and with highly crosslinked and complicated structures. The synthesis of linear and soluble polysilane, involve the condensation of monomer by Grignard reaction[14]. Polysilane was prepared from methyltrichlorosilane monomer in the presence of Mg in dry THF. The reaction mixture was refluxed for 8 h under Nitrogen atmosphere. The polysilane obtained was viscous liquid soluble in toluene. The polysilane was characterized by Gel Permeation Chromatography, FT- IR, ^{29}Si-CP-MAS NMR and ^{13}C CP-MAS NMR spectroscopy.



Scheme 1: Synthesis of polysilane

A pale yellow liquid polymer of molecular weight Mn = 1400, Mw = 1955 from GPC, using styrene as standard and toluene as solvent, was obtained.

5.2.1.1. FT-IR spectroscopy

Infrared spectrum of polycarbosilane showed usual bands at 2952, 2895 cm^{-1} which corresponded to the C-H stretching vibrations and Si-H vibration at 2089 cm^{-1}, bands at 1447 and 1252cm^{-1} were assigned to C-H antisymmetric and symmetric bends CH_3(-Si) of methyl groups, 863cm^{-1} due to the presence of CH_3 rocking, 777, 685 cm^{-1} bands correspond to the Si-C stretching. Band at 1045 cm^{-1} gives the evidence for the presence of Si-O–Si deformation.

5.2.1.2. ^{13}C-NMR spectrum

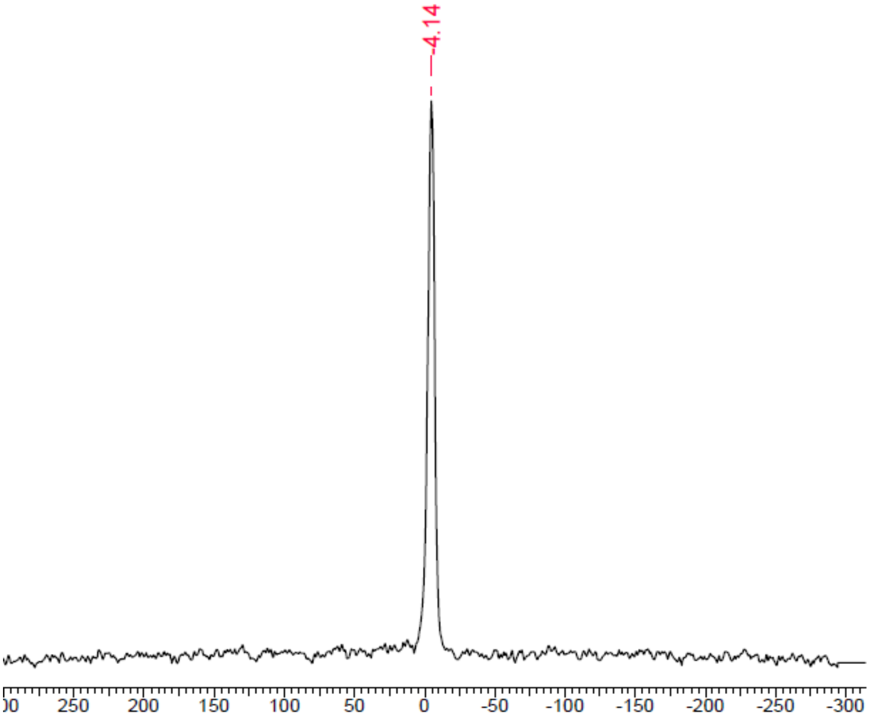


Figure 1: ^{13}C CP-MAS NMR spectrum of polysilane

The solid state ^{13}C NMR spectrum of PMS (shown in figure 1) exhibited only one resonance signal around -4.14 ppm, which was assigned to SiSiCH_3. The ^{13}C NMR spectrum of PMS indicates that it has only one type of carbon atom and also that it is attached to the Si atom.

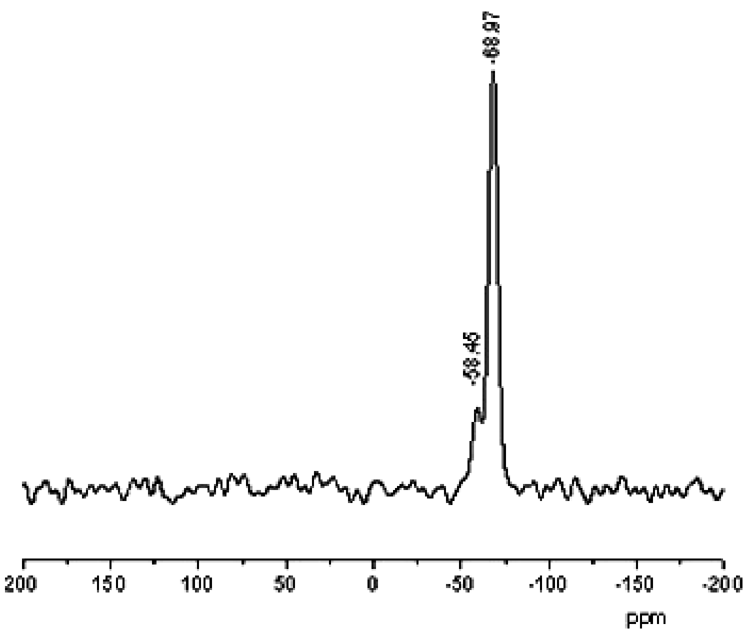


Figure 2: ^{29}Si CP-MAS NMR spectrum of polysilane

^{29}Si NMR spectrum of PMS is shown in Figure 2. Chemical shifts are based on tetramethylsilane as the internal standard. In the spectrum, the peak around -68.97 ppm was assigned to be due to the resonance of silicon in $(CH_3)\mathit{Si}Si$ unit (branching unit). A small peak in close proximity to it around -58.45 ppm is corresponding to the $(CH_3)Cl\mathit{Si}Si_2$ unit (linear unit). The branching unit was formed by the elimination of Cl atom from the Si-Cl groups during the synthesis.

5.2.1.3. Halide Estimation

The quantitative chlorine estimation of the polycarbosilanes was done by modified Volhard's method[15]. The chlorine estimation was done for polymethylsilane and the result is listed in table 1.

Table 1: Estimation of Chlorine content of polysilane

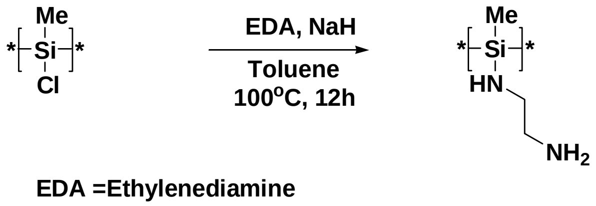
Polymer	PMS
Chlorine (mmol/g)	10.45

5.2.2. Synthesis of poly (propylene imine) dendrimer

Solid phase synthesis of poly (propylene imine) [PPI] dendrimer was carried out on chloro substituted polysilane[13]. The synthesis of the dendrimer was initiated by the conversion of chlorine groups into aminoethyl group by the reaction with ethylene diamine. The primary amino groups so obtained function as the core and also as the linker that connected the polysilane support and the dendrimer. PPI dendrimer was synthesized by double Michael addition of acrylonitrile to the amino groups of the polysilane support and followed by the reduction of the nitrile groups to amino groups using lithium aluminium hydride.

5.2.2.1. Introduction of amino group on polysilane

The polysilane with chlorine groups was converted into aminoethyl polysilane by the reaction with ethylene diamine in the presence of a base. This gave the polymer with an amino group with a small spacer of two carbon atoms in between the polymer and the amino group.



Scheme 2: Synthesis of aminofunctionalized polysilane

FT-IR spectra showed peak around 3694 cm $^{-1}$ due to stretching vibration of the primary amino group. The presence of amino groups was confirmed by the Ninhydrin test. The amino group estimation results showed that the polymer had 9.87 mmol/g of NH_2 groups.

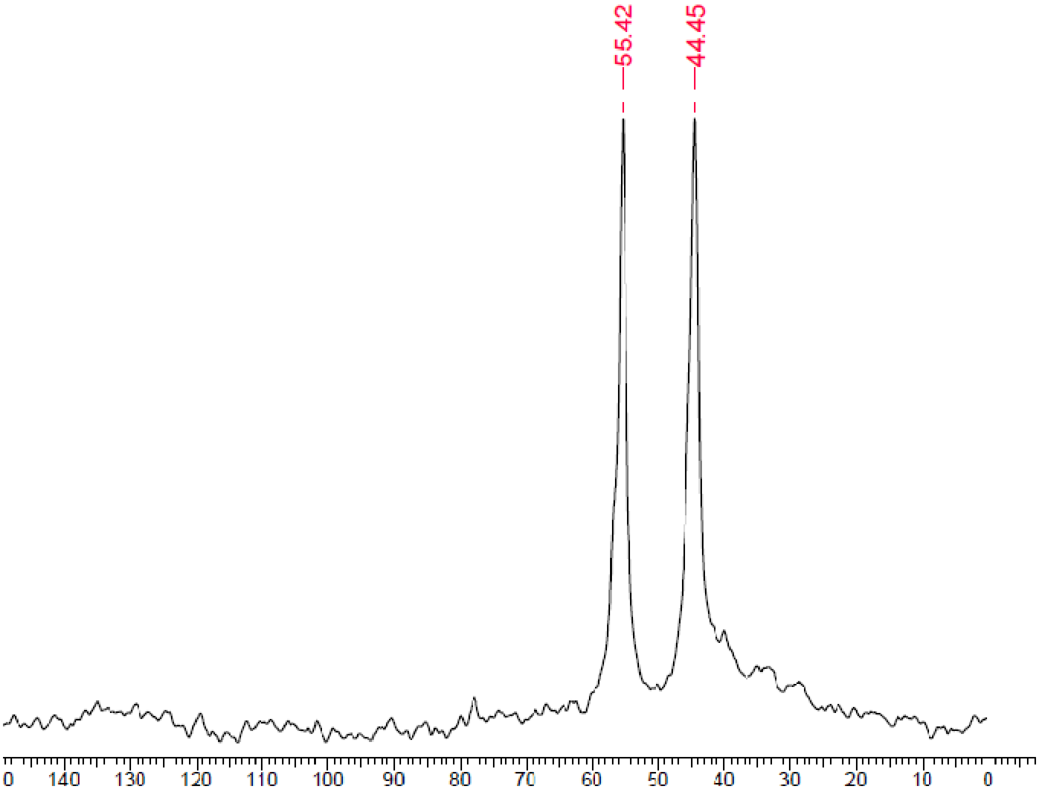
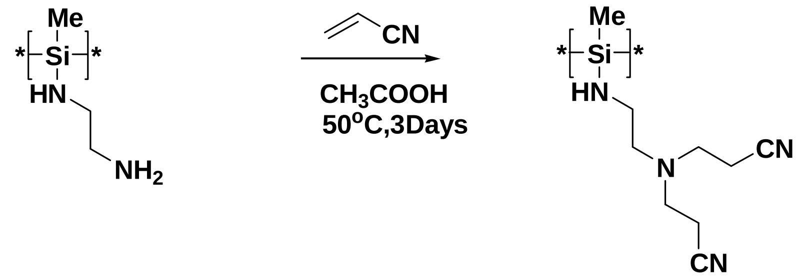


Figure 3: ^{13}C CP-MAS NMR spectrum of aminoethyl polysilane

The ^{13}C- NMR spectrum of aminoethyl polysilane gave two major peaks around 55.42 ppm and 44.45 ppm. The peak around 55.42 ppm is due to the resonance of Si-NH-$\underline{C}H_2$ and the peak around 44.45 ppm is obtained due to the resonance of Si-NH-CH_2-$\underline{C}H_2$-NH_2

5.2.2.2. Synthesis of G 0.5 PPI dendrimer

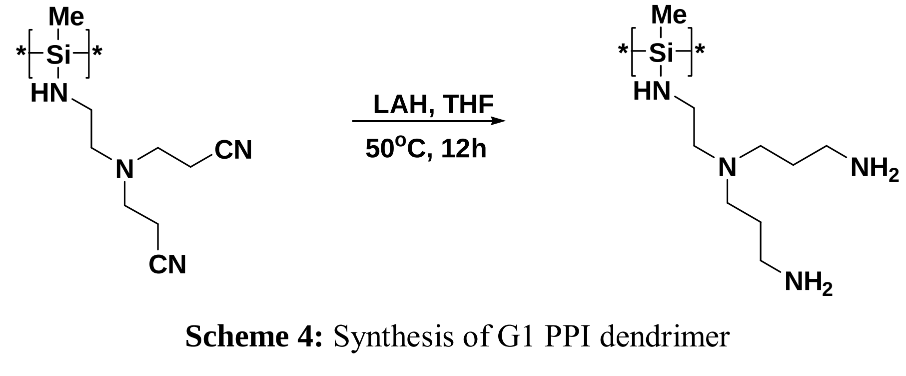
Acetic acid catalysed double Michael addition[6] was performed on the primary amino groups of the polysilane by acrylonitrile to get polysilane supported G 0.5 PPI dendrimer. The polymer was suspended in excess acrylonitrile so that the molar ratio of primary amino group to that of acrylonitrile was 1:100. The progress of the reaction was followed by FT-IR spectroscopy and Kaiser Ninhydrin test. FT-IR spectrum showed the appearance of a peak at 2249 cm^{-1} due to CN stretching vibration and the disappearance of the peak around 3694 cm^{-1}, due to the stretching vibration of amino groups of the polymer. Ninhydrin test also proved the disappearance of primary amino groups.



Scheme 3: Synthesis of G 0.5 PPI dendrimer

5.2.2.3. Synthesis of G1 PPI dendrimer

Synthesis of G1 PPI dendrimer was done by reducing the nitrile groups of polysilane supported G 0.5 PPI dendrimer to primary amino groups. The reduction was done using lithium aluminium hydride (LAH) in dry THF at 0 °C. Temperature was raised to 50 °C to ensure complete reduction. Generally, the reaction was completed with in 12 h. the reaction was followed by FT-IR spectroscopy and by Ninhydrin test. Product was characterized by FT-IR spectroscopy.

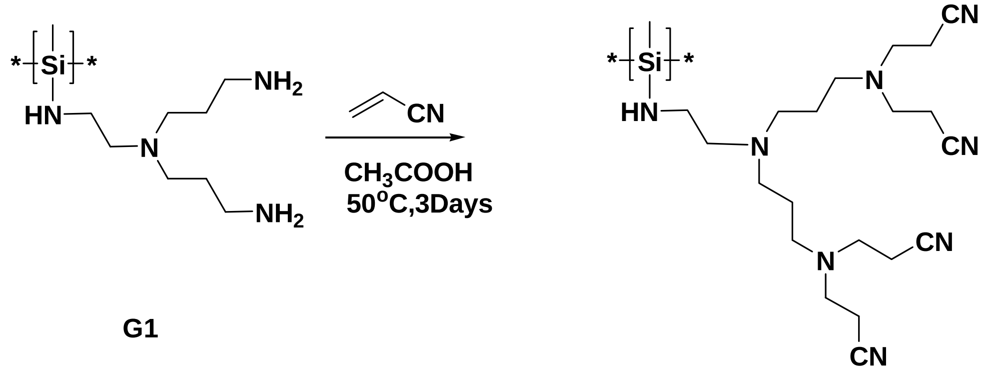


Scheme 4: Synthesis of G1 PPI dendrimer

The infrared spectrum showed a peak around 3593 cm^{-1} due to amino group stretching vibration and the disappearance of the peak around 2249 cm^{-1} which corresponded to the CN stretching. The amino group estimation result showed 18.90 mmol of amino groups per gram of the compound.

5.2.2.4. Synthesis of G 1.5 PPI dendrimer

The solid phase synthesis of G 1.5 dendrimer was done by acetic acid catalysed double Michael addition of acrylonitrile to the amino groups of polysilane supported G1 PPI dendrimer. The reaction conditions were as described in the synthesis of G 0.5 PPI dendrimer on polysilane. The reaction scheme is given below.



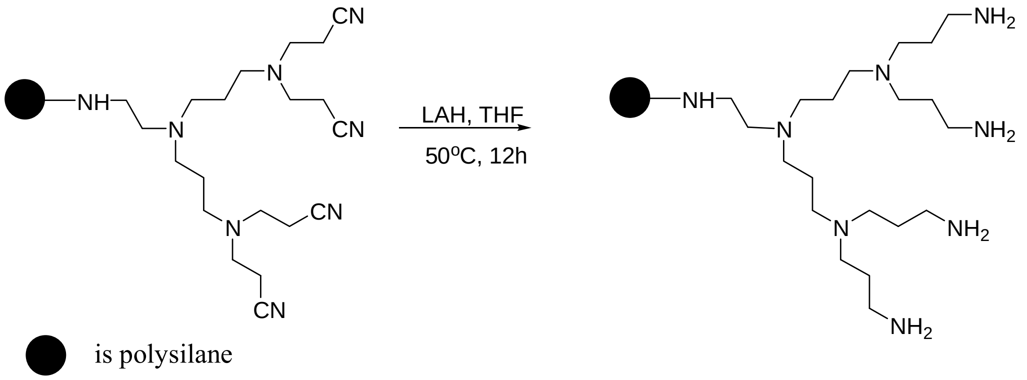
Scheme 5: Synthesis of G 1.5 PPI dendrimer

The progress of the reaction was followed by FT-IR and Kaiser Ninhydrin test. The reaction was continued till there was no purple colour for Ninhydrin test. FT- IR spectrum showed the appearance of a peak at 2254 cm^{-1} due to CN stretching vidrations and the disappearance of the peak at 3593 cm^{-1}, due to amino group stretching vibrations.

5.2.2.5. Synthesis of G 2 PPI dendrimer

The second generation PPI dendrimer was synthesized by the reduction of nitrile groups on G 1.5 dendrimer to primary amino groups using LAH in

THF. The reaction mixture was kept at 0°C for one hour. The temperature was slowly brought to 50°C for 12 h. The FT-IR spectra and Ninhydrin test showed the progress of the reaction. The completion of the reaction was confirmed by the disappearance of peak due to nitrile group and appearance of peak due to amino groups in the FT-IR spectrum.



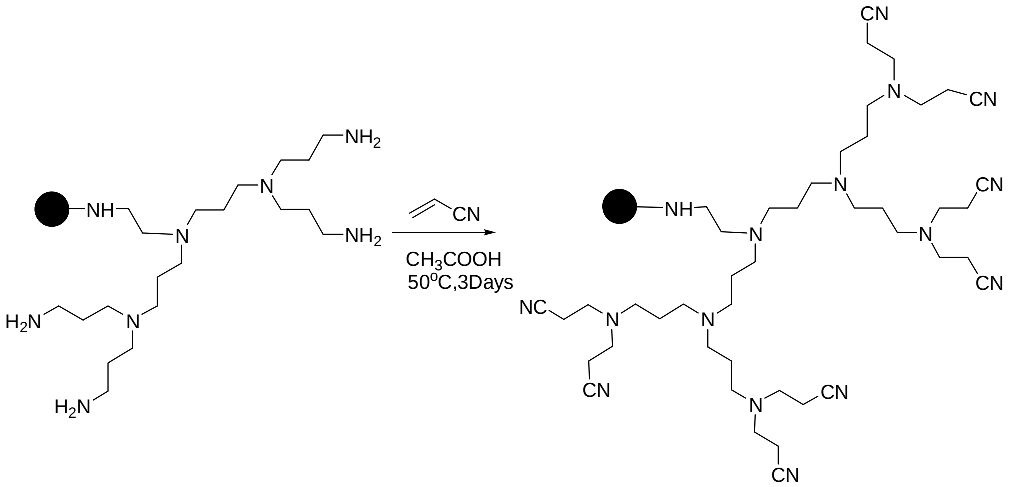
G2

Scheme 6: Synthesis of G 2 PPI dendrimer

The amino group estimation results also supported the progress of the reaction and showed that 37.54 mmol/g of amino groups were present in the compound.

5.2.2.6. Synthesis of G 2.5 PPI dendrimer

Michael addition of acrylonitrile to the amino groups of the second generation PPI dendrimer attached to the silicon polymer in the presence of glacial acetic acid gave G 2.5 generation PPI dendrimer. Acrylonitrile was taken in excess so that the molar ratio of primary amino group to that of acrylonitrile was 1:200. The progress of the reaction was followed by FT-IR spectra and Ninhydrin test. The reaction was conducted for 72 h, so that purple colour with Ninhydrin test was not obtained. The G 2.5 dendrimer on polysilane showed solubility in DMSO.



Scheme 7: Synthesis of G 2.5 PPI dendrimer

FT-IR spectrum showed the appearance of a peak at 2249 cm^{-1} due to CN stretching vibrations and the disappearance of amino peak at 3694 cm^{-1}.

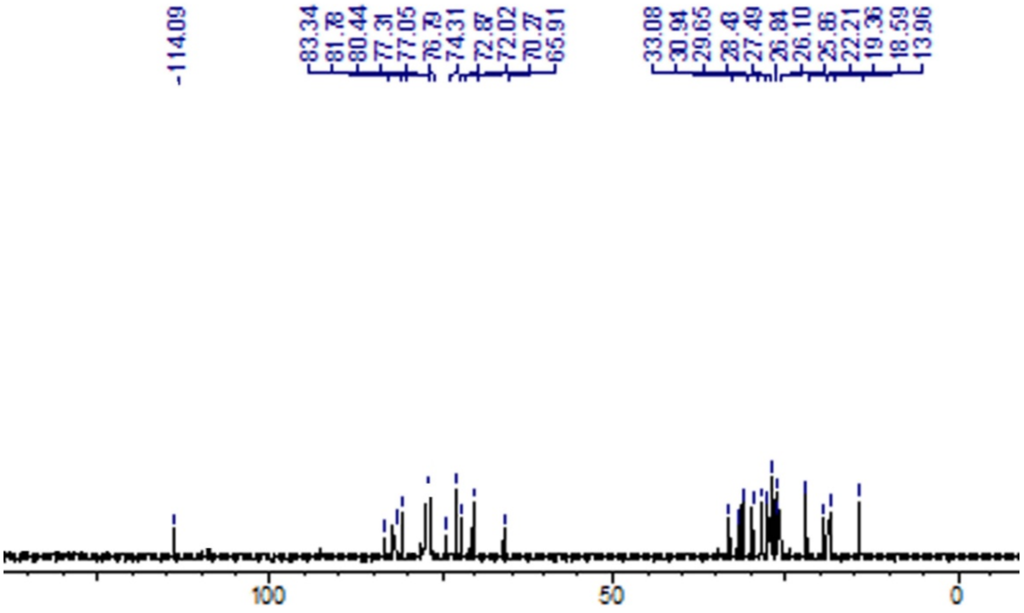
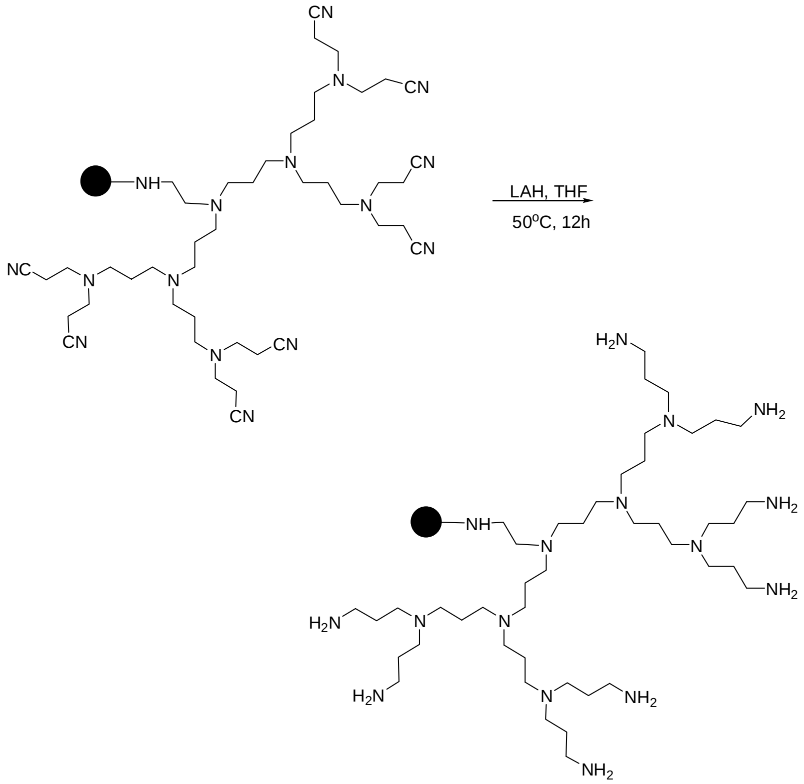


Figure 4: ^{13}C-NMR spectrum of G 2.5 PPI dendrimer on polysilane in DMSO-d_6

The ^{13}C-NMR spectrum showed peak around 114.09 ppm which was assigned due to the carbon in CN group. It confirms the product formation. The peaks around 70-60 ppm are due to the carbon atoms which are adjacent to the branching nitrogen atom. Peaks between 33 and 26 ppm are due to the carbon atom which lies in between two carbon atom linked to the nitrogen atoms. Peaks obtained around 19-18 ppm indicate the presence of carbon atoms which are attached to the nitrile group.

5.2.2.7. Synthesis of G 3 PPI dendrimer

Reduction of the nitrile groups of the G 2.5 dendrimer to primary amino groups by LAH in dry THF, gave G 3 PPI dendrimer. The reaction was followed by FT-IR spectra and Ninhydrin test. The completion of reaction was confirmed by the disappearance of peak at 2249 cm^{-1} due to CN group and the appearance of 3574 cm^{-1} peak. Ninhydrin test also gave a positive result.



G3

Scheme 8: Synthesis of G 3 PPI dendrimer

The presence of amino group was quantitatively determined for the G 3 PPI dendrimer, 75.79mmol/g of amino groups were present.

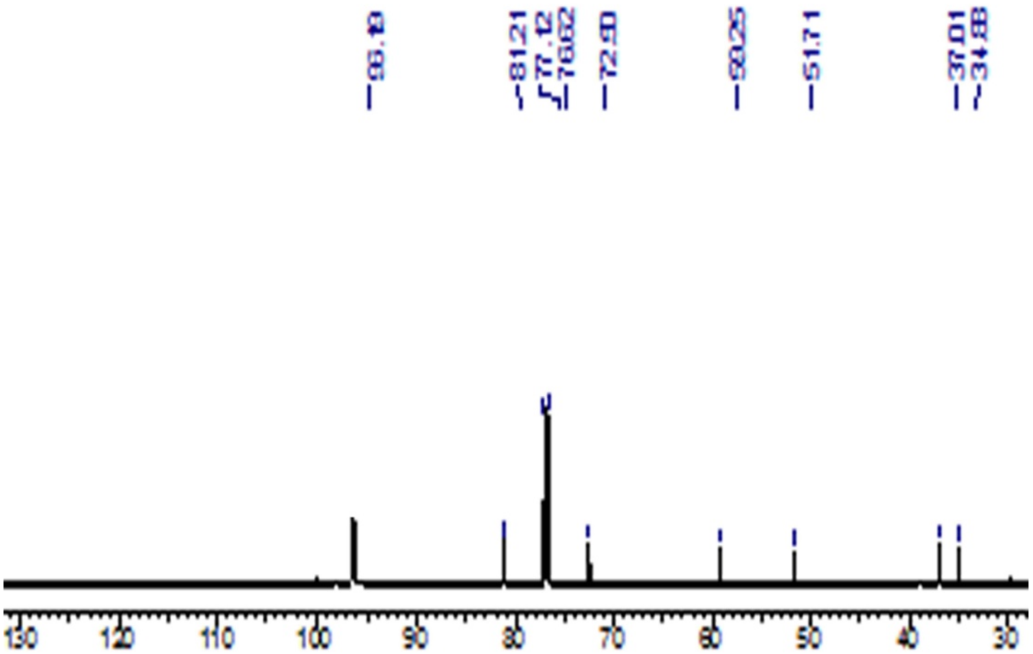


Figure 5: ^{13}C-NMR spectrum of G 3 PPI dendrimer on polysilane in DMSO-d_6

The ^{13}C-NMR spectrum gives an idea about the completion of reduction. The peak at 114 ppm, which corresponds to the peak of carbon of CN group, was absent indicating the complete reduction. Peaks obtained at 37 and 34 ppm are due to the carbon atoms which are adjacent to the primary amino group.

The proton NMR spectrum of polysilane which was functionalized with a third generation of PPI dendrimer is illustrated in figure 6.

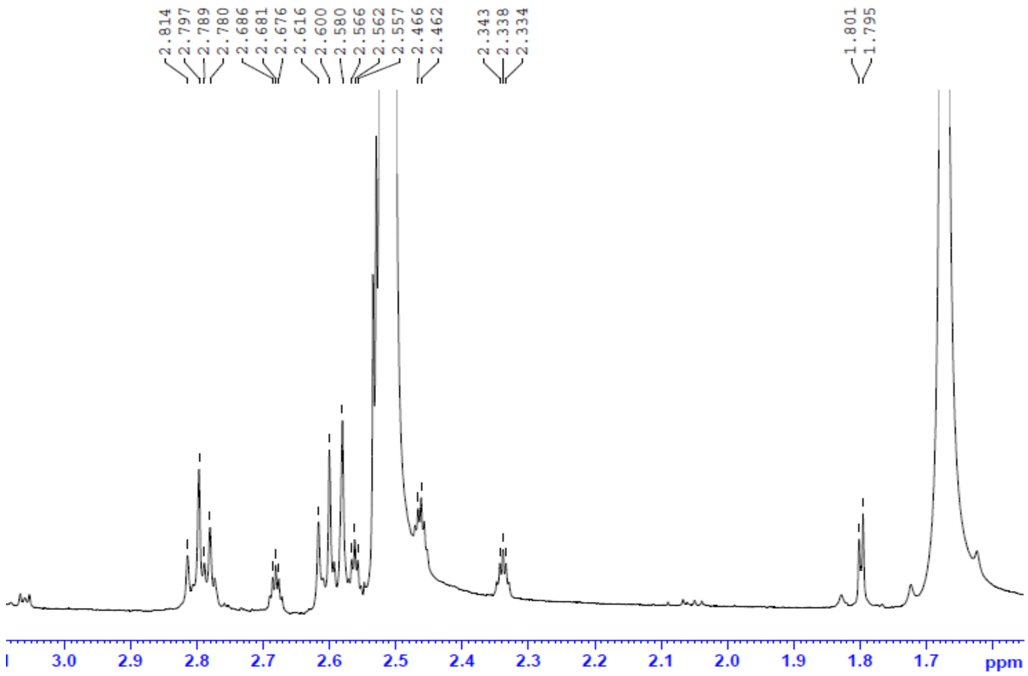


Figure 6: ^{1}H-NMR spectrum of G 3 PPI dendrimer on polysilane in DMSO-d$_6$

From the spectrum, it is clear that different types of hydrogen atoms are present in the compound. Peaks around 2.81-2.33 ppm indicate the presence of H-atoms connected to carbon which is linked to the branching nitrogen. Peaks around 1.80-1.79 ppm indicate the presence of Hs connected to cabrbon which lies in between two carbon atoms connected directly to the branching nitrogen.

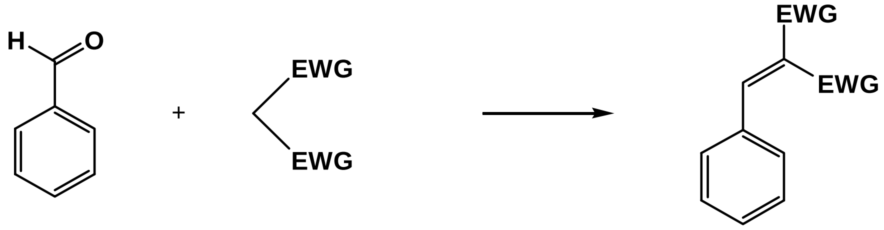
5.2.3. Catalytic activity study of polysilane supported PPI dendrimer

Catalytic transformations involving organic molecules, known as ‘organocatalysis’, have attracted much interest in recent years[16-19]. These catalysts are more environmental friendly, as they do not involve metals. The heterogenization of organocatalysts provides additional advantages, such as, the easy separation of the products and the reusability of the catalysts, which are very important in large scale production. Strategies involving the functionalization of both inorganic and polymer supports with organocatalysts have been reported[20].

5.2.3.1. Knoevenagel condensation reaction

The catalytic activity of polysilane supported PPI dendrimers (PS-PPI) was studied by taking Knoevenagel condensation reaction. The reaction is a well known classical reaction of condensation between carbonyl compounds and compounds containing active methylene group catalysed by bases like amines[19,21-27]. Various solid acid catalysts and solid-supported catalysts have been applied for this reaction. Anion-exchange resin, amino group immobilized silica materials, clays and alkali and alkaline earth carbonates[28-34] have also been reported.

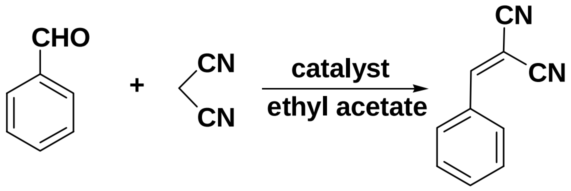
An equimolar mixture of carbonyl compound and active methylene compound with 5 mol% of catalyst was taken. The reaction was stirred at requisite temperature for 30 min; after the completion of the reaction, the reaction mixture was filtered. The catalyst was washed with ethyl acetate. The solvent was evaporated and the percentage conversion of each of the products was analyzed by HPLC with a solvent ratio, ($CH_3OH:H_2O$) as 70:30. The product formed was recrystallised from ethyl acetate and compounds have been identified by comparison of spectral data with those previously reported (FT-IR, ^1H NMR spectra and mass spectra by LC-MS) and melting point.



Scheme 9: Knoevenagel condensation reaction

5.2.3.2. Optimization of reaction condition

In order to quantify the catalytic performance of the PPI dendrimer attached on polysilane, reaction between benzaldehyde and malononitrile, was carried out under various reaction conditions.



Scheme 10: Knoevenagel condensation reaction with benzaldehyde and malononitrile

Initially, the reaction time was optimized. Equimolar concentrations of the carbonyl compound and active methylene compound were reacted in the presence of 5 mol % of dendrimer attached polysilane in ethyl acetate. The results are presented in table 2.

Table 2: Optimization of reaction time*

Entry	Reaction time (min.)	Mol% of catalyst	Conversion (%)
1	5	5	79
2	10	5	93
3	15	5	100

*0.05mol aldehyde, 0.05mol compound with active methylene group, temp-30^{o}C, solvent-ethyl acetate.

From the results it is seen that reaction was completed within 15 min. under specified reaction conditions. It was chosen as the optimum reaction time for Knoevenagel condensation reaction.

The molar concentration of the catalyst was optimized. Equal concentrations of the carbonyl compound and active methylene compound were reacted in the presence of different mol % of dendrimer attached polysilane in ethyl acetate. The results are given in table 3.

Table 3: Optimization of amount of catalyst*

Entry	Mol% of catalyst	Conversion (%)
1	2	85
2	3	95
3	5	100

*0.05mol of substrates, solvent-ethyl acetate, temp- 30°C, time-15 min.

From the results obtained, it is clear that the optimum amount of catalyst for the Knoevenagel condensation reaction under given conditions is 5 mol%.

The catalytic activity of the PPI dendrimer functionalised polysilane was established by conducting the reaction with diverse set of substrates, which are listed in table 4. The known compounds have been identified by comparison with those previously reported spectral data (FT-IR, ^{1}H NMR and mass spectra from LC-MS) and melting point.

Table 4: Knoevenagel condensation reaction with different substrates*

Entry	Carbonyl compound	Active methylene compound	Temp. (°C)	Conversion (%)
1	Benzaldehyde	Malononitrile	30	100
2	Anisaldehyde	Malononitrile	30	98
3	4-Chlorobenzaldehye	Malononitrile	30	100
4	4- Hydroxybenzaldehyde	Malononitrile	30	100
5	4-(Dimethylamino)benzaldehyde	Malononitrile	30	98
6	Benzaldehyde	Ethylcyanoacetate	50	95
7	Anisaldehyde	Ethylcyanoacetate	50	95
8	4-Chlorobenzaldehye	Ethylcyanoacetate	50	98
9	4- Hydroxybenzaldehyde	Ethylcyanoacetate	50	96
10	4-(Dimethylamino)benzaldehyde	Ethylcyanoacetate	50	92

*Reaction condition: 0.05mol aldehyde, 0.05mol compound with active methylene group, solvent-ethyl acetate, 5 mol% PS-PPI and Time-15 min.

The PPI dendrimer attached polysilane gave high yield for all the substrates. Hence it can be considered as a good catalyst for Knoevenagel condensation reaction.

5.2.3.3. Recycling of catalyst

Reuse of catalyst was performed as follows: Knoevenagel condensation of benzaldehyde and malononitrile; was carried out under optimized reaction conditions. Results are entered in table 5.

Table 5: Recycling catalyst *

No. of cycles	Time (min.)	Conversion (%)
1	15	100
2	15	98
3	15	95
4	15	91

*0.05mol of substrates, solvent-ethyl acetate, 5 mol% PS-PPI, temp- 30°C and Time-15 min.

It was observed that the PS-PPI retained its form and characteristics after the completion of the reaction. Also they have all the advantages of solid phase catalysts including operational simplicity, filterability, regenerability and reuse. There was no considerable difference in the reactivity after recycling.

5.3. Conclusion

PPI Dendrimer functionalized polysilane was prepared. The synthesis included two parts; initial step was the synthesis of polysilane. It was synthesized from the monomer trichloromethylsilane. Subsequently the functionalization of polysilane with PPI dendrimer by divergent method was carried out. The polysilane was characterized by GPC, FT- IR, ^{29}Si-CP-MAS NMR and ^{13}C CP-MAS NMR spectroscopy. The polysilane supported PPI dendrimer upto the third generation was prepared. Michael addition and reduction were used in succession to synthesize PPI dendrimer. The polysilane functionalized with dendrimer was characterized by FT-IR, ^{29}Si-CP-MAS NMR, ^{13}C NMR spectroscopy and amino group estimations were carried out in each generation. The results confirmed the preparation of dendrimer functionalised polysilane. The catalytic activity of PPI dendrimer immobilized polysilane was studied. Knoevenagel Condensation Reaction was selected to study the catalytic activity. Reaction conditions were optimized. It was found that the PPI dendrimer functionalized polysilane showed high catalytic activity.

5.4. Experimental

5.4.1. Preparation of polysilane

In a 250 mL round bottom flask, Magnesium (1.03 g, 42.36 mmol) in anhydrous THF (50 mL) was refluxed and stirred vigorously to make a dispersion. Trichloromethylsilane (5 mL, 42.36 mmol) was added drop wise. The reaction was highly exothermic. After the addition of monomers, the reaction mixture was refluxed for 8 h. The whole process was carried out under Nitrogen atmosphere. The reaction mixture was cooled and the suspension obtained was filtered and solvent was removed by fractional distillation. The prepared polysilane was characterized by FT- IR spectroscopy, ^{29}Si-CP-MAS NMR, solid state ^{13}C-NMR.

5.4.2. Estimation of chlorine capacity

Halide analysis was done by the modified Volhard's Method.The polymer (250mg) was heated in pyridine (2.5mL) for 1 h at 100^{o}C, and the suspension was diluted with acetic acid: water (1:1) (25mL). The halide was displaced by the addition of HNO_3 (5mL) and precipitated with a measured excess of standard $AgNO_3$ solution. AgCl that was formed was coated with toluene, and the excess $AgNO_3$ was back titrated with standard NH_4SCN solution, using ferric alum [$FeNH_4(SO_4).12H_2O$] as an indicator. A red colour due to the formation of $Fe(SCN)_3$, indicated that an excess of SCN^- was present and that the end-point had been reached.

5.4.3. Introduction of amino group on polysilane

The prepared polysilane (5g) was taken in a 250 mL round bottom flask with 50 mL toluene. After adjusting the temperature to 0 °C, Ethylendiamine (28 mL) was added dropwise to the reaction mixture and followed by 1 g of Sodium hydride (paraffin colloid was washed with hexane and dried) as base. The reaction mixture was stirred at 0 °C for 1 h and the temperature was allowed to rise to the room temperature and refluxed for 12 h to ensure the completion of the reaction. The reaction mixture was cooled and ethyl acetate was added to it to destruct the excess sodium hydride. It was filtered, washed with ethyl acetate, methanol, 5% KOH solution, water and then with methanol. The polymer was dried under vacuum for 24h. Amount of amino group per gram of the resin was estimated.

5.4.4. Estimation of amino group

The ethylene diamine attached polysilane (100 mg) was suspended in standard hydrochloric acid (40 mL) for 24h with occasional stirring. The resin was filtered and washed well with distilled water. The filtrate and the washings were collected. The unreacted hydrochloric acid was estimated by titration against standard Na_2CO_3 solution using methyl orange as indicator. A blank titration was also carried. From these values, the amount of amino groups per gram of the resin was calculated.

5.4.5. Procedure for Michael addition of acrylonitrile

The aminoethyl polysilane (2g) was added in portions to a mixture of acrylonitrile (4 mL) and glacial acetic acid (1 mL) with constant stirring. The reaction mixture was kept at 50 °C with stirring for three days. The reaction mixture was filtered and washed with 5% $NaHCO_3$ solution and followed by washing thoroughly with water, methanol and acetone. The polymer was dried under vacuum. The polymer was analyzed with ^{13}C-NMR, FT-IR spectroscopy.

5.4.6. Procedure for the reduction of nitrile group to amino group

The above obtained polymer was suspended in dry THF taken in a 100mL R.B. flask kept at 0°C in an ice bath. A slurry of LAH in dry THF was added dropwise to the reaction mixture with stirring. The reaction mixture was kept at 0°C for one hour. The temperature was slowly brought to 50°C and stirred for 12 h to ensure complete reduction. Excess LAH was removed by adding ethyl acetate. It was filtered and washed with THF, diethylether, THF-dil.HCl, dil.HCl, water, methanol, and acetone. The resin was dried under vacuum. The amino group was qualitatively detected by Ninhydrin test.

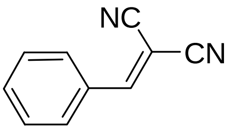
The two steps of Michael addition and subsequent reduction using LAH was continued to obtain G3 PPI dendrimer on polysilane

5.4.7. Study of Catalytic Activity

5.4.7.1. Knoevenagel condensation reaction

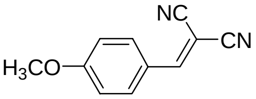
An equimolar mixture of carbonyl compound and active methylene compound with polysilane supported dendrimer catalyst (5 mol% of amino groups with respect to the substrates) was taken with 10 mL ethylacetate in a 25 mL round bottom flask. The reaction mixture was stirred at room temperature (reaction with ethyl cyanoacetate was performed at 50°C) for 12 h and it was filtered and washed with ethyl acetate. Solvent was removed in a rotator flash evaporator and washed with water. The product formed was recrystallised from ethyl acetate. All the products were analysed with HPLC (Column: C18) in a solvent ratio (CH_3OH:H_2O) of 70:30. The products were known compounds and identified by comparing the spectral data (FTIR, ^{1}HNMR, and mass spectra by LCMS) and melting points with those reported. The analytical details are listed below.

Entry 1: [2-Benzylidenemalononitrile], $C_{10}H_6N_2$



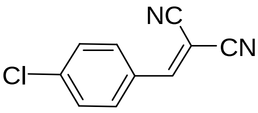
LCMS ES$^+$ (M$^+$+1) m/z: 155; **FTIR (KBr,** cm^{-1}): 2220, 1557; **H^1-NMR (400MHz, CDCl$_3$)** δ : 8.10 (m, 1H), 7.92 (m, 1H), 7.90 (m, 1H), 7.78(s, 1H), 7.54 (t, 2H); **M.p**.: 81-82°C.

Entry 2: [2-(4-Methoxybenzylidene)malononitrile]- $C_{11}H_8N_2O$



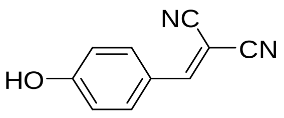
LCMS ES$^+$ (M$^+$+1) m/z: 185; **FTIR (KBr,** cm^{-1}): 2218, 1557; **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.92 (m, 2H), 7.65 (s, 1H), 7.02 (m, 2H), 3.91 (s, 3H); **M. p.:**109 - 110°C.

Entry 3: [2-(4-Chlorobenzylidene)malononitrile]- $C_{10}H_5ClN_2$



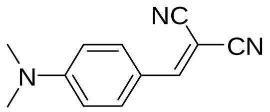
LCMS ES$^+$ (M$^+$+1) m/z: 189; **FTIR (KBr,** cm^{-1}): 2230, 1540; **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.86 (m, 2H), 7.73 (s, 1H), 7.51 (m, 2H); **M. p.**: 154°C.

Entry 4: [2-(4-Hydroxybenzylidene)malononitrile]- $C_{10}H_6N_2O$



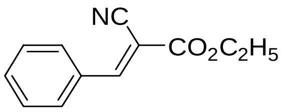
LCMS ES^+ (M^++1) m/z: 171; **FTIR (KBr,** cm^{-1}**)**: 3450, 2358, 1416; **H^1-NMR (400MHz, $CDCl_3$)** δ: 7.88 (m, 2H), 7.64 (s, 1H), 6.97 (m, 2H), 6.37 (bs, 1H); **M. p**.: 182 °C.

Entry 5: [2-(4-(Dimethylamino)benzylidene)malononitrile], $C_{12}H_{11}N_3$



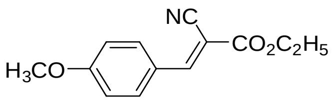
LCMS ES^+ (M^++1) m/z: 198; **FTIR (KBr**, cm^{-1}): 2932, 2358, 1647, 1516, 1320, and 1087. **H^1-NMR (400MHz, $CDCl_3$)** δ: 7.82 (m, 2H), 7.46 (s, 1H), 6.71 (d, 2H), 3.16 (s, 6H). **M. p**.:177-180°C.

Entry 6: [Ethyl 2-cyano-3-phenylacrylate]- $C_{12}H_{11}NO_2$



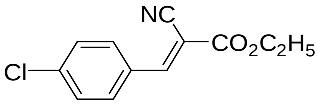
LCMS ES^+ (M^++1) m/z: 202; **FTIR (KBr,** cm^{-1}**)**: 2932, 2358, 1747, 1416, and 1087; **H^1-NMR (400MHz, $CDCl_3$)** δ: 8.12 (m, 2H), 7.63 (m, 1H), 7.48 (m, 2H), 4.40 (q, 2H), 1.40 (t, 3H); **M. p**.: 52 °C.

Entry 7: [Ethyl 2-cyano-3-(4-methoxyphenyl)acrylate]- $C_{13}H_{13}NO_3$



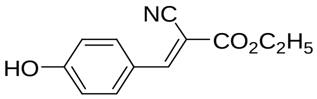
LCMS ES^+ (M^++1) m/z: 232; **FTIR (KBr,** cm^{-1}**)**: 2982, 2358, 1704 and 1040; **H^1-NMR (400MHz, $CDCl_3$)** δ: 8.08 (m, 2H), 6.96 (m,3H), 4.08 (q, 2H), 3.41 (s, 3H), 1.17 (t, 3H); **M. p**.: 90 °C.

Entry 8: [Ethyl 3-(4-chlorophenyl)-2-cyanoacrylate]- $C_{12}H_{10}ClNO_2$



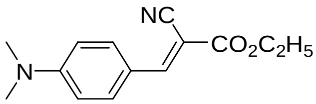
LCMS ES^-(M^+-1) m/z: 234; **FTIR (KBr,** cm^{-1}**)**: 2932, 2358, 1747, 1416, 1320; **H^1-NMR (400MHz, $CDCl_3$)** δ: 8.05 (m, 2H), 7.94 (d, 1H), 7.47 (m, 2H), 4.40 (q, 2H), 1.40 (t, 3H); **M. p.:**162-164°C.

Entry 9: [Ethyl 2-cyano-3-(4-hydroxyphenyl)acrylate]- $C_{12}H_{11}NO_3$



LCMS ES$^+$ (M$^+$+1) m/z: 218; **FTIR (KBr,** cm^{-1}**)**: 3445, 2932, 2358, 1747, and 1047; **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.82 (m, 2H), 6.99 (m, 3H), 4.42 (q, 2H), 1.89 (bs, 1H), 1.39 (t, 3H); **M. p.**: 169-170°C.

Entry 10: [Ethyl 2-cyano-3-(4-(dimethylamino)phenyl)acrylate]- $C_{14}H_{16}N_2O_2$



LCMS ES$^+$ (M$^+$+1) m/z: 245; **FTIR (KBr,** cm^{-1}**)**: 2932, 2358, 1747, 1416, 1320, and 1087; **H^1-NMR (400MHz, CDCl$_3$)** δ: 7.75 (d, 2H), 6.7 (d, 3H), 4.34 (q, 2H), 3.1 (s, 6H), 1.37 (t, 3H); **M. p.**: 65-70°C.

5.4.7.2. Optimization of amount of catalyst

An equimolar mixture of benzaldehyde and malononitrile was reacted in the presence of polysilane supported dendrimer as catalyst. Reaction with 2, 3 and 5 mol% of catalyst was taken in to consideration. The reaction mixture was stirred for 15 min at room temperature.

5.4.7.3. Reuse of catalyst

Reuse of catalyst was performed as follows: Knoevenagel condensation reaction of benzaldehyde and malononitrile was carried out under optimized reaction condition. After completion of the reaction the catalyst was removed from the reaction mixture by filtration and washed thoroughly with ethyl acetate, methanol and acetone and dried under vacuum for 24 h. The process was repeated in each cycle.

5.5. References

1. Twyman, L. J.; King, A. S. H.; Martin, I. K. *Chem.Soc. Rev.*, **2002**, *31*, 69.
2. Astruc, D.; Boisselier, E.; Ornelas, C. *Chem. Rev.* **2010**, *110*, 1857.
3. Kim, C.; Hong, J. H. *Molecules* **2009**, *14,* 3719.
4. Nguyen, T. T. T.; Turp, D.; Wang, D.; Nolscher, B.; F. Laquai, F.; Mullen, K. *J. Am. Chem. Soc.* **2011**, *133*, 11194.
5. Feher, F. J.; Wyndham, K. D.; Knauer, D. J. *Chem. Commun.* **1998**, 2393.
6. Klajnert, B.; Bryszewska, M. *Acta Biochimica Polonica*, **2001**, *48*, 199.
7. Delgado, M.; Janda, K. D. *Current Organic Chemistry*, **2002**, *6*, 1031.
8. Krishnan, G. R.; Sreekumar, K. *Polymer*, **2008**, *49*, 5233.
9. Lee, J. W.; Kim, B. K.; Kim, H. J.; Han, S. C.; Shin, W. S.; Jin, S.H. *Macromolecules*, **2006**, *39*, 2418.
10. King, A. S. H.; Twyman, L. J. *J. Chem. Soc. Perkin Trans.1*, **2002**, 2209
11. Krishnan, G. R.; Sreekumar, K. *Applied Catalysis A: General*, **2009**, *353*, 80.
12. Buhleier, E.; Wehner, W.; Vögtle, F. *Synthesis*, **1978**, 155.
13. Liu, P.; Wu, X.; Pu, Q.; Su, Z. Anal. Chim. Acta*,* ***2005****,* 95*, 695*.
14. Birot, M.; Pillot, J.P.; Dunogues, J. *Chem. Rev.* **1995**, *95*, 1443.

15. Yan, B.; Czarnik, A. W.; Dekker, M. '*Optimization of Solid- Phase Combinatorial Synthesis*' **2002** New York, Marcel Dekker.
16. Han, J.; Xu, Y.; Su, Y.; She, X.; Pan, X. *Catal. Commun.* **2008**, *9,* 2077.
17. Heerbeek, R. V.; Kamer, P. C. J.; Leeuwen, P. W. N. M. V.; Reek, J. N. H. *Chem. Rev.* **2002**, *102*, 3717.
18. Astruc, D.; Chardac, F. *Chem. Rev.* **2001**, *101*, 2991.
19. Reddy, K. R.; Rajgopal, K.; Maheswari, C. U.; Kantam, M. L. *New J. Chem.* **2006**, *30*, 1549.
20. Kapoor, M. P.; Kasama, Y.; Yokoyama, T.; Yanagi, M.; Inagaki, S.; Nanbu, H.; Juneja, L. R. *J. Mater. Chem.* **2006**, *16*, 4714.
21. Krishnan, G. R.; Thomas, J.; Sreekumar, K. *ARKIVOC*, **2009**, x, 106.
22. Yamashita, K.; Tanaka, T.; Hayashi, M. *Tetrahedron,* **2005**, *61*, 7981.
23. Goa, Y.; Wu, P.; Tatsumi, T. *J. Catal.* **2004**, *224*, 107.
24. Hassan, V.; Hamid, G. *Synthetic Commun.* **2010**, *40*, 1477.
25. Georgeta, P.; Biswajit, C.; Bikash, K.; Kumari, P.; Julie, B.; Aline, A. *J. Catal.* **2010**, *269*, 110.
26. Prajapati, D.; Sandhu, J. S. *J. Chem. Soc. Perkin Trans. 1*, 1993, 739.
27. Liao, J.; Wang, Q. *Macromolecules,* **2004**, *37*, 7061.
28. Hein, R. W.; Astle, M. J.; Shelton, J. R. *J. Org. Chem.* **1961**, *26*, 4874.
29. Corma, A.; Fornes, V.; Martin-Aranda, R. M.; Garcia, H.; Primo, J. *Appl. Catal.* **1990**, *59*, 237.
30. Linares, C.F.; Goldwasser, M.R.; Machado, F.J.; Rivera, A.; Fuentes, G. R.; Barrault, J. *Micropor. Mesopor. Mater.* **2000**, *41*, 69.

31. Shinkai, S.; Araki, K.; Shibata, J.; Manabe, O. *J. Chem. Soc. Perkin Trans-1*, **1989**, 195.

32. Choudary, B. M.; Lakshmi Kantam, M. L.;Sreekanth, P.; Banopadhyay, T.; Figueras, F.; Tuel, A. *J. Mol. Catal. A* **1999**, *142*, 361.

33. Rao, Y. V. S.; Choudary, B. M *Synth. Commun.* **1991**, *21*, 1163

34. Aramendia, M. A.; Borau, V.; Jimenez, C.; Marinas, J. M.; Romero, F. J. *Chem Lett.* **1995**, 279.

Chapter 6

SUMMARY AND CONCLUSION

In modern synthetic organic chemistry, the development of efficient reagent or catalyst recycling systems is regarded as one of the most important topics. The use of polymer supports is one of the potential approaches for this purpose, and the immobilization of reagents or catalysts on polymer supports offers a number of important advantages over their traditional homogeneous counterparts. The immobilization of transition metals on polymer supports offers a number of advantages over traditional solution-phase chemistry. In an ideal case, the supported complexes can be recovered from reaction mixtures by simple filtration, they do not contaminate the product solution, they can be recycled, and they can help increase selectivity.

Polysilanes are polymers having silicon backbone with organic substituents. Variation of substituents and copolymerization of different dichlorodiorganosilanes offers countless possibilities for tailoring chemical and physical properties, e.g., solubility, morphology, and optical activity. Functionalized polysilanes have found application in the field of catalysis.

Polycarbosilanes (PCS) are rather neglected class of polymers which contain both Si and C in their backbone structure. This class of polymers can be compared to the existing classes of inorganic and organic polymers; they possess a combination of low t_g’s and high synthetic versatility similar to polyphosphazenes and polysiloxanes and with good chemical backbone stability similar to that of polyolefins. Polycarbosilanes can represent structural hybrid between polysilanes and polyolefines, which have found applications as liquid crystals, SiC-precursor and catalyst; recently considerable interest has been focused on it.

The present thesis has described the development of heterogeneous catalysts based on polycarbosilane and polysilanes. The functionalization of these silicon polymers produced heterogeneous catalysts. These functionalized silicon polymers were used as catalysts in selected reactions. The catalysts show recyclability and the reaction conditions used were environmentally friendly.

The thesis is divided in to six chapters. An overview of solid phase organic synthesis, and also a thorough review of silicon polymers, particularly polysilanes and polycarbosilanes were included in the **first chapter**.

In **Chapter 2** synthesis of five polycarbosilanes was discussed. Five polycarbosilanes were prepared. Trichloromethylsilane, chlorodimethylvinylsilane, diethoxymethylvinylsilane and trimethoxyvinylsilane were used as monomers. The preparation involved the Wurtz-type coupling reaction of monomer molecules in the presence of metallic sodium. The polycarbosilanes were characterised using various analytical techniques such as UV-Vis DRS, TG-DTA, X-ray diffraction analysis, FT-IR spectroscopy, ^{13}C NMR spectroscopy, ^{29}Si NMR spectroscopy and surface area analysis. From the results of analytical data the structure of polycarbosilanes were deducted. All the polycarbosilanes were of highly crosslinked structure and amorphous in nature. All of them possessed high temperature stability and high surface area. Halogen estimation was done by Volhard's method. The polycarbosilanes, except PCS5, were capable of further functionalization. The functionalization of polycarbosilanes could be done to make use of the polycarbosilanes in a variety of applications.

Chapter 3 has dealt with the polycarbosilane supported transition metal ions, their synthesis and characterization. Metal salts of Ti (IV), Mn (II), Co (II), Ni (II), Cu (II) and Pd (II) were used for the metal ion attachment. The reaction conditions were optimized. The metal attached polycarbosilanes were characterized using various analytical methods. The spectroscopic techniques used are FT-IR, UV-Vis DRS, ^{29}Si-CP-MAS NMR, ^{13}C CP-MAS NMR, EPR spectroscopy and TG/DTA, magnetic susceptibility measurements, BET surface area analysis and AAS/ICP-AES.

The catalytic activity of transition metal ions attached to polycarbosilane supports were studied. The details were discussed in **Chapter 4.** Organic reactions like Biginelli reaction, Knoevenagel condensation reaction, Mannich reaction and Heck reaction were taken into consideration for the study. Effect of PCS support on the catalytic activity was investigated. The reaction conditions were optimized and recycling of catalysts was examined. It was observed that high surface area is a supportive aspect for the application of polycarbosilane in catalysis.

Chapter 5 has disussed the synthesis and application of dendrimer functionalized polysilanes. PPI Dendrimer was functionalized on polysilane support. The synthesis included two parts; initial step was the synthesis of polysilane. It was synthesized from the monomer trichloromethylsilane. Subsequently the functionalization of polysilane with PPI dendrimer by divergent method was carried out. The polysilane was characterized by GPC, FT- IR, ^{29}Si-CP-MAS NMR and ^{13}C CP-MAS NMR spectroscopy. The polysilane supported PPI dendrimer upto the third generation was prepared. Michael addition and reduction were used in succession to synthesize the PPI dendrimer. The polysilane functionalized with dendrimer was characterized by FT-IR, ^{29}Si-CP-MAS NMR, ^{13}C NMR spectroscopy and amino group estimations were carried out in each generation. The results confirmed the formation of dendrimer functionalised polysilane. The catalytic activity of PPI dendrimer immobilized on polysilane was studied. Knoevenagel Condensation Reaction was selected to study the catalytic activity. The reaction conditions were optimized and recycling of catalysts was examined. It was found that the PPI dendrimer functionalized polysilane was a reusable catalyst with high activity. The important observations of the study are presented in the last chapter.

◆