Pt-Nanoparticle Catalysis: Applications in Transformations of Silicon Containing Monomers and Polymers

By

Alok Sarkar

A dissertation submitted to the graduate Faculty in Chemistry in partial fulfillment of the requirement for the degree of Doctor of Philosophy, The City University of New York

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This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy

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Abstract

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By

Alok Sarkar

Advisor: Professor Bhanu P. S. Chauhan

My thesis dissertation mainly involves investigation of catalytic efficiency of Pt-nanoclusters in various transformations including hydrosilylation and hydrogermylation of functional alkynes, hydrolytic oxidation of organosilanes and functionalization of polybutadienes. Hydrosilylation and hydrogermylation of various functional alkynes were studied in presence of Pt-nanoclusters. Studies revealed that Pt-nanocluster possesses excellent catalytic activity in both hydrosilylation and hydrogermylation reactions tolerating the presence of variety of functional group on the alkynes such as –NH_2, COOH, -CN, -F, -OMe etc. The catalytic activity of Pt-nanoclusters on the hydrolytic oxidation were studied using a variety of functional mono and di-hydrosilanes, where most of the hydrosilanes smoothly converted to corresponding silanols without formation of detectable amount siloxanes. Functionalization of polybutadienes was achieved using Pt-nanoclusters catalyzed hydrosilylation reactions. A series of important functional groups such as linear, cyclic and polyhedral oligosiloxane and ferrocene were successfully introduced into the polymers. The microstructures and thermal properties of the functionalized polymers were characterized using multinuclear NMR, GPC and TGA-DTA studies. The morphology of these polymers was investigated using various EM

techniques (TEM and SEM) and AFM. The studies revealed self-assembled nanostructured formation with ferrocene and siloxy functionalized polymers.

I dedicate this dissertation to my parents, who provided me love, encourage and enormous support to complete my doctoral research.

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A. Sarkar

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Chapter 1

1. Transition Metal Nanoclusters

The metal nanoclusters typically of less than 10 nm in diameter have generated intense interest over the past few decades. The modern "transition metal nanoclusters" are distinguished from traditional colloids by several important factors. Recently, several criteria have been summarized by Finke to distinguish modern nanoclusters from traditional colloids such as the control over the composition, size, solubility, isolability and redissolvability.[1] Specifically, nanoclusters are expected to be smaller (1-10 nm) with near-monodisperse size distributions, while colloids are often >10 nm with much broader size distribution. Additionally, modern nanoclusters will have reproducible syntheses leading to compositionally well-defined, isolable and redissolvable nanoclusters. Traditionally colloids have less well-defined compositions along with less reproducible syntheses.

Due to their size-related unique properties, metal nanoparticle have many fascinating potential uses, including catalysis,[2] quantum dots[3] or quantum computers,[4] chemical sensors,[5] light-emitting diodes,[6] industrial lithography[7] many other photochemical applications.[8] Owing to their extremely large surface area, transition metal nanoclusters have been used as active catalysts for many organic transformations. Transition metal nanoclusters catalysis currently became a central field of nanoscience and nanotechnology.[9] The use of nanoparticles in the catalysis first appeared in 19th century with the photography (AgNPs) and decomposition of hydrogen peroxide

(PtNPs).[10] In 1940s, Nord and coworker reported the pioneering applications of nanoparticles in catalysis, where they have shown potential application of Pd and Pt-nanoparticles in catalytic hydrogenation of nitrobenzenes.[11] In 1970, Parravano and coworker have reported catalytic hydrogen-atom transfer from cyclohexane to benzene and oxygen-atom transfer from carbon dioxide to carbon monoxide using Au-nanoparticles.[12] In a related work, Haruta and coworkers used oxide supported Au-nanoparticle for the oxidation of carbon monoxide in presence of oxygen at low temperature.[13] In 1970s, a number of publications also appeared describing Au-nanoparticle catalyzed olefin hydrogenations.[14] In 1990s, Reetz and coworkers found potential catalytic application of Pd-nanoparticles in carbon-carbon bond-forming reaction via Heck coupling.[15] In case of hydrosilylation, Lewis and coworker demonstrated the colloidal mechanism based upon the observation of nanoparticle formation during the catalysis of olefin hydrosilylation using organometallic complexes of Pt, Pd, Ni and Co.[16-17]

1.1. Advantages of nanoclusters as soluble metal particle catalysts

The use of nano-materials as catalysts for chemical reaction represents an important bridge between homogenous and heterogeneous processes.[9b] Lipophilic or hydrophilic metal nanoclusters, dissolved in the form of organosols or hydrosols can serve as catalysts in organic solutions and in the aqueous phase, respectively. Schmid has referred these reactions, which involve solvated metal atom dispersions as 'heterogeneous catalysis in solution'.[18]

While heterogeneous catalysis is responsible for the largest volume of production due to the recyclability of the catalysts, homogeneous catalysis has significant impact in

terms of selectivity thus adding tremendous value to the chemical industry. Therefore, the soluble metal nanoclusters, which can be treated as "soluble analogues of heterogeneous catalysts", present the unique combination of properties of both homogeneous and homogeneous catalysts.

The nanoclusters are often more active under mild conditions than corresponding supported metal particle catalysts.[18] This must be due the number and type of the active sites present, which is a function of the conditions under which the catalysts are typically prepared. Traditional heterogeneous catalysts are typically prepared at high temperatures, which causes annealing to the most stable surface structure. A second advantage of soluble nanocluster catalysts is that they have been found to be more selective than corresponding traditional heterogeneous catalysts for some reactions. It has been demonstrated that the clusters provide low-energy pathways, which lead to reactions with high selectivity to products.[19]

The two main factors that contribute to the potential of nanoclusters to be more active and selective catalysts than classical heterogeneous catalysts are; (i) a large percentage of metal atoms that lie on the surface of nanoclusters, (ii) the electrons in a nanocluster are confined to a very smaller volume, giving rise to quantum size effects.[20]

1.2. Synthesis and Stabilization of transition metal nanoclusters.

Generally there are two basic approaches for the formation of metal nanoclusters; (a) "top-down" and (b)"bottom-up" approach (Figure 1).[21] The "top-down' approach involves the thermal, chemical, or mechanical fragmentation or dispersion of a bulk metal followed by the stabilization of the generated nanoclusters with appropriate stabilizing agents. The more common "bottom-up" approach involves generating the nanocluster by

decomposition (usually chemical reduction) of organometallic precursors to their neutral free metal. The stabilization of the free metal nanoparticles is achieved with a chemical agent to confine the clusters in the nanosize regime.

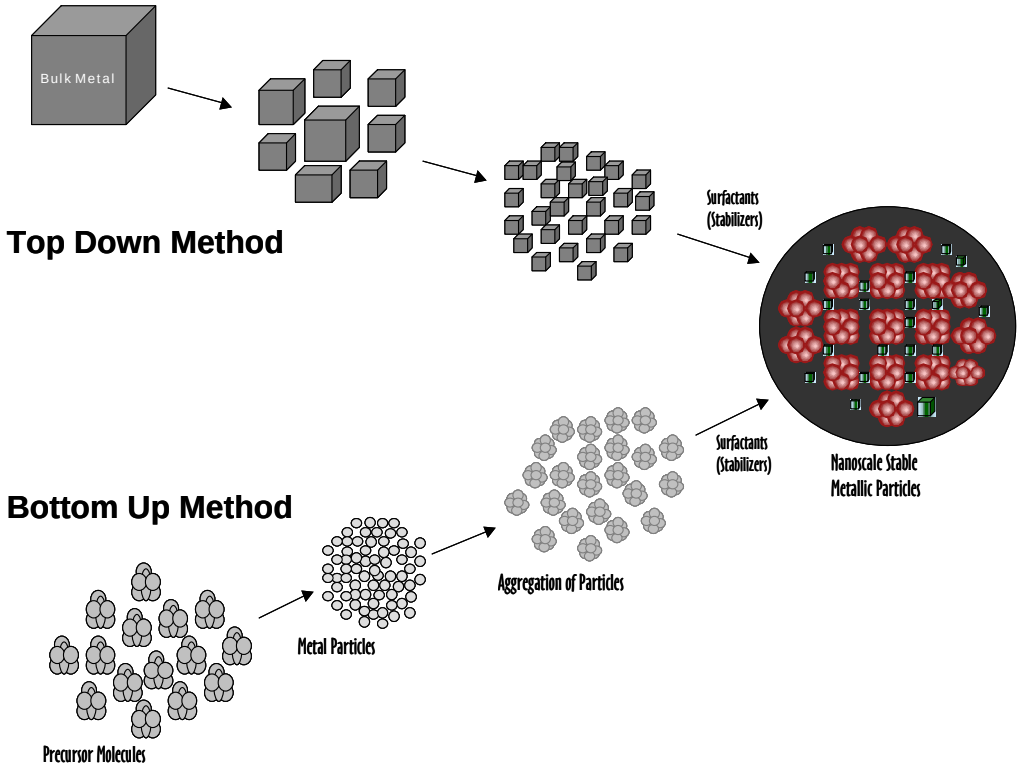


Figure 1. Two approaches: (a) top-down and (b) bottom-up methods for the synthesis of nanoparticles (adopted from Ref 21).

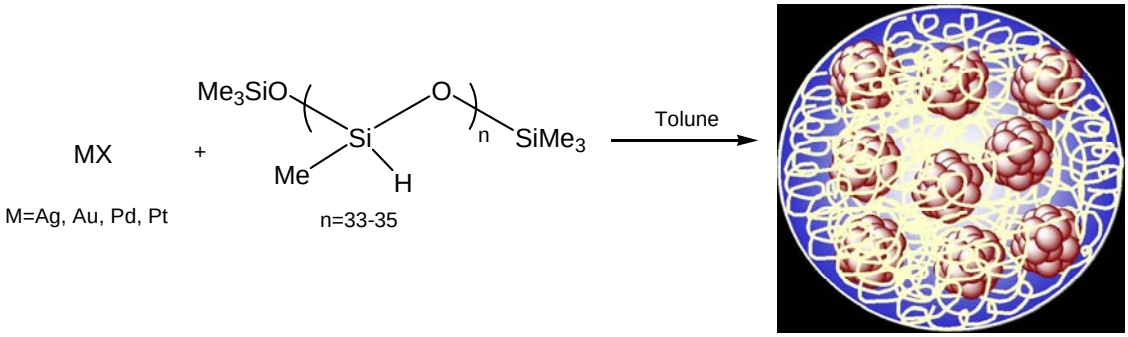
The nanoclusters that are dissolved in solution must be stabilized using a protective agent in order to prevent them from agglomeration. In general, there are two modes of stabilization; (i) electrostatic stabilization and (ii) steric stabilization.[22] The electrostatic stabilization occurs when anions (halides, carboxylates or polyoxyanions etc.) attach to the unsaturated surface metal atoms of the metal particles leading to the formation of electrical double-layers. This produces a Coulombic repulsion between the nano-object. The steric stabilization is where sterically hindered organic molecules are used as protective shell against agglomeration of metal particles.

Since the discovery of metal nanoparticle synthesis by Michael Faraday,[23] nanoparticles has been produced by chemical reduction of corresponding metals salts in solution in the presence of suitable stabilizing agents including polymers,[24] block co-polymers,[25] dendrimers,[26] solvents such as THF,[27] MeOH,[28] and propylene carbonate,[16c] long-chain alcohols,[29] surfactants,[16b-c,25a,30] and organometallics.[31] As described above, the presence of these coordination ligands strongly passivated the surface of the nanoparticles and most often makes them catalytically inefficient. There has been body of research where coordinating polymers such as polyvinylpyridines (PVP), polyols, etc., have also been used for stabilizing the metal nanoparticles. However, in most cases the catalytic activity of such nanoparticles diminishes because of the limited access to the metal surface.

1.3. Objective of My Doctoral Dissertation

Over the past five years, our group has been exploring the novel strategy for the synthesis, stabilization and application of various transition metal nanoclusters.[32] Our strategy for the preparation of metal nanoclusters is based on our hypothesis that the aggregation of the nanoclusters (meatballs) can be prevented if enough flexible polymeric material (spaghetti) is present to physically wrap the particle during their formation process.[32f] Due to very weak physical interactions imparted by the flexible polymers, such type nanoclusters are expected to show superior activity in comparison to nanoclusters passivated by strong coordinating ligands. Using this strategy, a number of well-defined metal particles including Ag, Au and Pd nanoparticleswere synthesized (Scheme 1) and successfully utilized in the generation of self–assembled nanomaterials[32d]

and also as potential catalysts in macromolecular grafting via silaesterification and alcoholysis reactions.[32a-c]



Scheme 1. '*Meatball-Spaghetti*" strategy to synthesize nanosize metal particles.

Most recently, our group has synthesized polymethyl hydrosiloxane (PMHS) stabilized Pt-nanoclusters and studied their catalytic activity in macromolecular grafting of polysiloxanes via regioselective hydrosilylation of olefinic bonds. These Pt-nanoclusters have shown many potential applications over the classical homogeneous metal complexes in terms of selectivity, recyclability and ease of product purification.[32e,h,i] As platinum based complexes comprise one of the most important classes of catalysts used for variety of organic and inorganic transformations, we tried to further explore the catalytic activity of this newly developed Pt-nanocluster catalysts with the following objectives. (i) to investigate the catalytic activity of Pt-nanoclusters in hydrosilylation and hydrogermylation of functional alkynes. (ii) to investigate the catalytic activity of Pt-nanoclusters in hydrolytic oxidation of organosilanes. (iii) to explore application of Pt-nanoclusters catalyst for the synthesis of silyl-functional polyolefins and their characterizations. (iv) to study the nature of the catalysts during various catalysis.

(i) Investigation of the catalytic activity of Pt-nanoclusters in hydrosilylation and hydrogermylation of functional alkynes. Vinylmetallic species such as vinylsilanes and vinylgermanes are widely used building blocks in various organic transformations.[33] Because of this, synthesis of stereo and regio-defined vinylmetallic species with a range of functionalities is highly desirable. Metal catalyzed hydrosilylation/hydrogermylation of alkynes is a very versatile methodology, which can lead to such vinylmetallic species.[34] Although significant progress has been made in hydrosilylation/hydrogermylation catalysis, very limited number of reports has appeared which describe selective hydrosilylation[34a-d] and hydrogermylation[34o-p] of disubstituted functional alkynes with high selectivity. Recent developments in the catalysis research have demonstrated unusual chemical and physical properties of transition metal nanoparticles as recyclable and green catalysts.[35] However, systematic studies of nanoparticle catalysis in the field of hydrogermylation and hydrosilylation of alkynes have not been reported. Therefore, investigation of Pt-nanoclusters catalyzed hydrosilylation and hydrogermylation of functional alkynes became one of the objectives of my research.

(ii) Investigation of the catalytic activity of Pt-nanoclusters in hydrolytic oxidation of organosilanes. Organosilanols are important precursors for organic transformations[36] and are widely applied building blocks in industry for production of silicon containing polymeric materials[37]. A number of preparative procedures for the silanol have been developed, however most of the methodologies including hydrolysis of chlorosilanes,[38] oxidation of organosilanes with stoichiometric amounts of oxidants[39] and treatment of siloxanes with alkali metal reagents,[40] have limited scope because of the formation of

undesirable siloxane byproducts. This is because silanols are highly sensitive towards siloxane formation even in presence of trace amount of acid or base. Although the oxidation of organosilane using transition metal-complex catalysis[41] has shown a promising selectivity, very limited number of reports has appeared in the literature[41e-f] describing a mild hydrolytic procedure for silanol synthesis. Pt-nanoclusters, which are free of either acidic or basic ligands, may find potential application as catalysts for selective silanols formation. Driven by this interesting opportunity, we decided to investigate the catalytic activity of Pt-nanoclusters in the hydrolytic oxidation of organosilanes.

(iii) Application of Pt-nanoclusters catalyst for the synthesis of silyl-functional polyolefins and the characterization of the products. Silicon-functionalized polyolefins have received considerable attention both scientifically and technologically because of their potentials applications as rubber materials, adhesives and biomaterials (drug carriers).[43] The well-known hydrosilylation reactions on unsaturated polymers, offers a useful and convenient method to silicon-functionalized polyolefins. Although much progress has been achieved in the olefin-hydrosilylation reactions using various Lewis acid and transition metal catalysts, very limited reports are known to describe the hydrosilylation of polyolefins.[44] Moreover, most of the reported methods experience severe limitations such as low selectivity, lack of catalyst recyclability and difficulty in complete removal of catalyst. So, another objective of my thesis was to synthesize silicon-functionalized polyolefins via hydrosilylation of polybutadienes using Pt-nanocluster catalysis.

(iv) The study of the exact of nature of the catalysts during various catalytic reactions. The identification of the active metallic species during the transition-metal catalyzed homogenous/heterogeneous reactions is an important topic of fundamental research and has led to a number of seminal publications.[42] There are some fundamental differences in the physical and chemical properties of the classical homogenous catalysts when compared with nanocluster catalysts. For example, a true homogenous catalyst typically has single type of active sites whereas the metal particles have multiple types of active sites on their surfaces. Consequently, the catalytic properties such as catalytic activity, selectivity and recyclability are greatly influenced by the nature of the catalyst species. Determination of the true nature of the catalysts is thus highly desirable from the viewpoints of both fundamental research and the commercial catalytic process development. Therefore, investigation of the true nature of the catalysts during the catalysis was crucial in our study.

1.4. Synthesis and Characterization of Pt-nanoclusters

In a typical procedure, a platinum metal salt, $Me_2Pt(COD)$ (COD: 1,5 cyclooctadiene) (0.25 mmol, 0.084 g) was taken in a 100 mL round bottom flask connected to nitrogen flow. To this solid, toluene (50 mL) and polymethylhydrosiloxane (PMHS) (Mw≈ 2000) (10.0 mmol, 0.60 mL) were added under the continuous flow of nitrogen. The reaction mixture was then allowed to stir at 80 ^{0}C under positive pressure of nitrogen. After 0.5 h, the color of the reaction mixture turned yellow. In order to monitor the reduction process, an aliquot of the reaction mixture was taken out and analyzed by UV-vis spectroscopy. After 24 h of the reaction the complete reduction of Pt-complex was indicated by disappearance of UV absorption peak (≈320 nm) corresponding to the $Me_2Pt(COD)$

(Figure 2). After confirming the complete reduction of $Me_2Pt(COD)$, an aliquot (1 mL) of the dark solution was diluted with freshly distilled toluene (2 mL). One drop of this diluted solution was deposited on carbon/formvar-coated copper grids and analyzed by transmission electron microscopy (TEM). The TEM images showed Pt-nanoparticles are present in the black solution (Figure 3). The particle size analysis of the TEM image indicated formation of nearly monodisperse particles with the average size of 3.00 nm (figure 3).

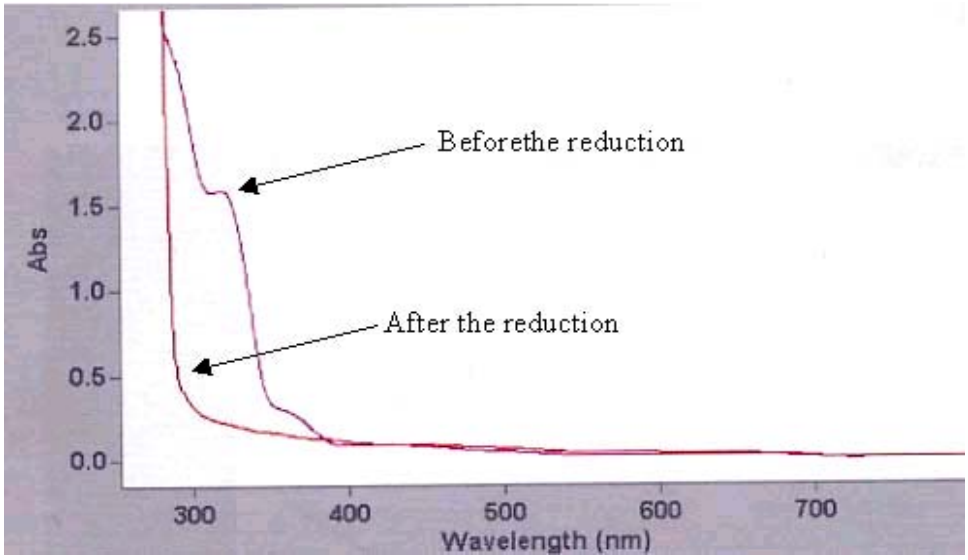


Figure 2. UV-vis analysis showing spectrum before and after the reduction of $Me_2Pt(COD)$.

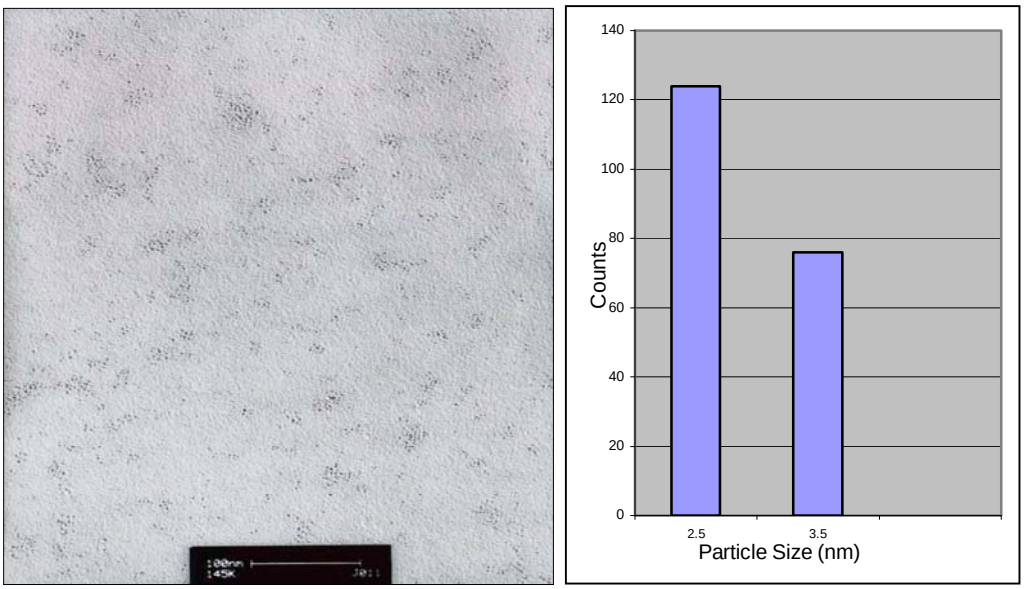


Figure 3. TEM image of polysiloxane conjugated Pt-nanoclusters solution.

After confirming the presence of Pt-nanoparticle, the flow of nitrogen was stop and the reaction mixture was exposed to air under stirring. A gummy brown-black solid was formed within 6 h. This gummy solid was collected on a filter paper and washed thoroughly with toluene. Air-drying this gummy solid furnished black powder (referred to as Pt-nanoclusters) was further characterized using various techniques.

1.5. Characterization of Pt-nanoclusters

In the past 60 years, a number of techniques for the characterization of nanoparticle have been developed. The combination of these techniques can provide the complete morphological, structural and chemical information about metal nanoparticles. The current techniques, which are extensively used in this field includes: transmission electron microscopy (TEM), scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron microscopy (XPS), extended X-ray absorption fine structure (EXAFS), X-ray diffraction (XRD), Multinuclear NMR, UV-vis and IR spectroscopy. To get the structural and chemical insight about the Pt-nanoclusters, the

solids were characterized using TEM, SEM, EDS, XPS, NMR, and UV-vis and IR techniques.

1.5.1. SEM and EDS Analysis of Pt-nanoclusters

Scanning electron microscopy (SEM) is a useful technique to study nanoparticles and nanoparticle systems. It can provide morphological information of specimen with nanometer resolution. Scanning electron microscopy when combined with energy dispersive X-ray spectroscopy (EDS) techniques, it is possible to find out the distribution of various elements in the nanoclusters.

To analyze Pt-nanocluster using SEM, a sample was prepared by directly depositing the powdered nanoclusters on aluminum holder with carbon-tab and coating with carbon vapor to make sample conducting. The SEM analysis of this sample revealed spherical morphology of polysiloxane conjugated Pt-nanoclusters with an average diameter of 50 nm (Figure 4). The distribution of several elements in the nanoclusters was also studied using EDS analyzer attached to the SEM instrument. The EDS analysis of the considered sample showed 2.3 weight % of platinum metal uniformly dispersed throughout the solid (figure 5). Three different batches of nanoclusters were also analyzed by SEM and EDS to know if there is any variation in the morphology and composition. Although a slight variation was observed in the platinum content (4-6 weght %) no significant difference was observed in morphology. The composition of the elements in the solid was further verified by elemental analysis, which has showed 4-5 weight % of platinum metal is present in the solid (Table 1).

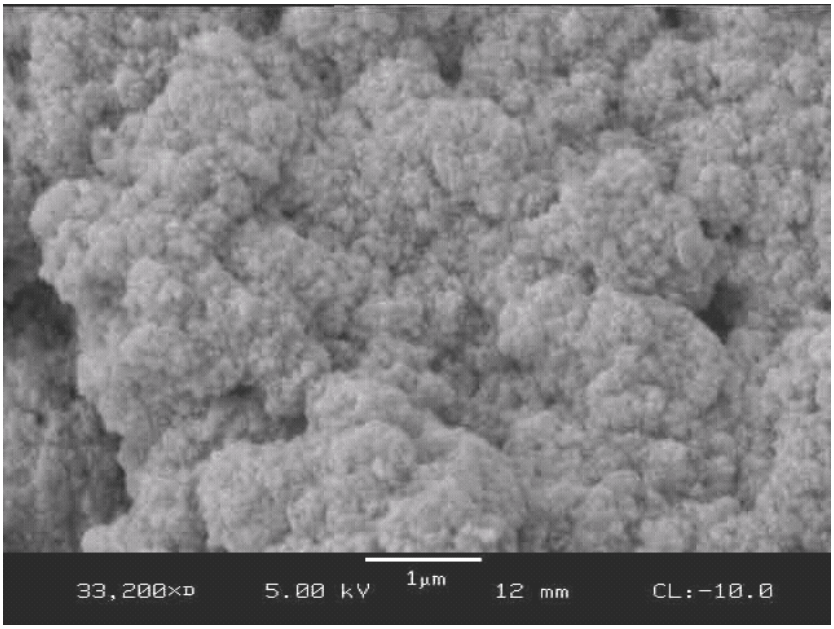
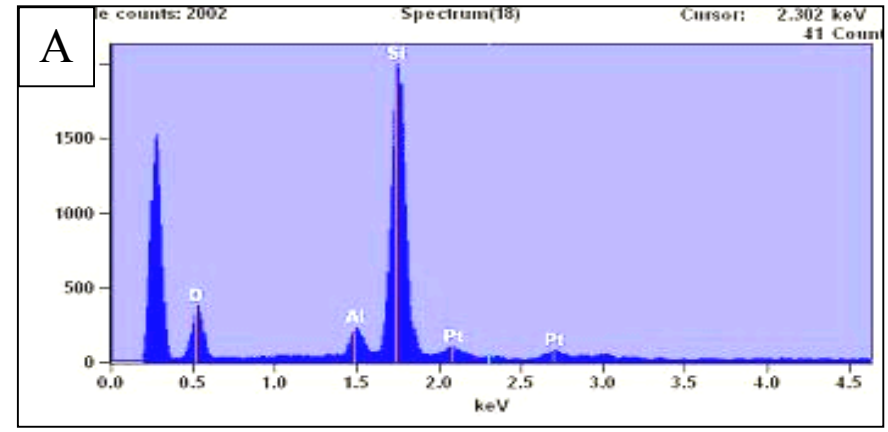


Figure 4. SEM images of the Pt-nanoclusters



Element	Net counts	ZAF	Element Wt %	Atom %
O K	2049	4.046	37.75	52.28
Al K	1797	2.595	5.32	4.37
Si K	21225	2.575	54.61	43.08
Pt L	856	0.752	2.31	0.26
Total			100.00	100.00

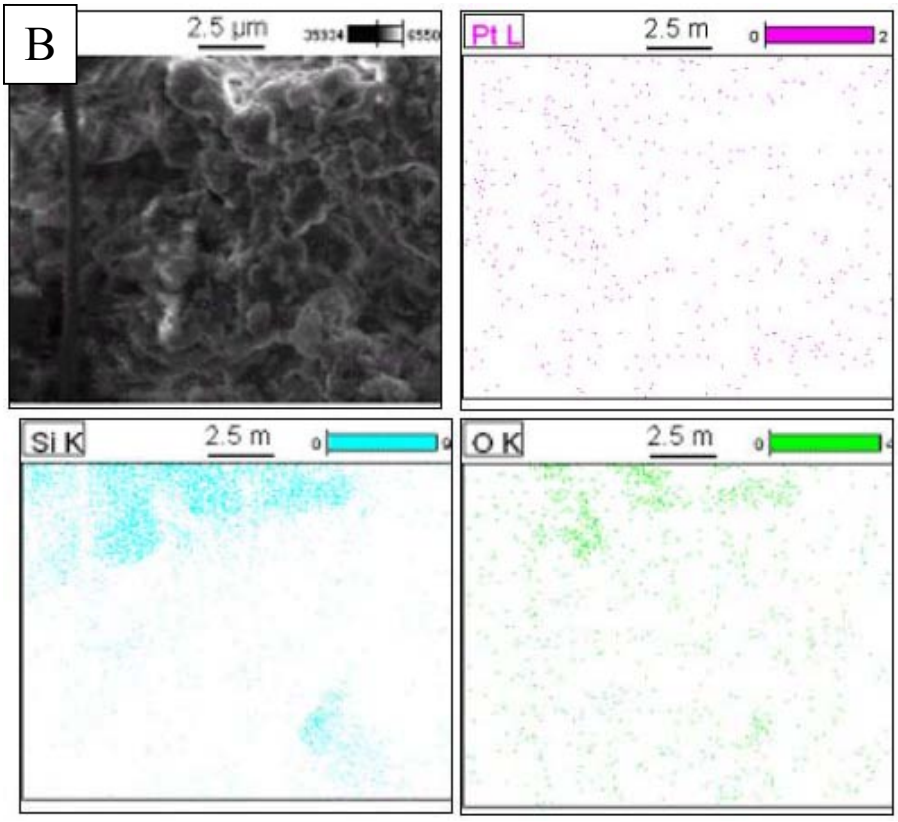


Figure 5. (A) EDS Spectra and table of composition. (B) X-ray mapping showing distribution of different elements in the solids.

Table 1. Elemental analysis data for Pt-nanoclusters.

Batch	Element Analyzed	Method of Analysis	Results (wt %)
1	Silicon	ICP-OES/FLAA/ GFAA/ ICP-MS	34.5
	Platinum	ICP-OES/FLAA/ GFAA/ ICP-MS	5.01
	Carbon	ASTM D5373/ D5291	20.35
	Hydrogen	ASTM D5373/ D5291	4.56
	Oxygen		35.58
2	Silicon	ICP-OES/FLAA/ GFAA/ ICP-MS	34.1
	Platinum	ICP-OES/FLAA/ GFAA/ ICP-MS	3.91
	Carbon	ASTM D5373/ D5291	15.85
	Hydrogen	ASTM D5373/ D5291	4.75
	Oxygen		41.39

1.5.2. X-ray Photoelectron Spectroscopy (XPS) of Pt-nanoclusters

X-ray photoelectron spectrometer (XPS) plays an outstanding role in investigation of surface composition and depth profile of chemical composition in material science. In XPS, X-ray photons of well defined energy impact the sample and eject photoelectrons from the atomic core level and valence levels and by analyzing the energy of such ejected photoelectrons, a spectrum is obtained in terms of intensity vs. binding energy. The binding energy of these photoelectrons depends on the surface area as well as nature and oxidation state of the elements. Therefore, by looking at the spectra one can easily predict about nature and the oxidation state of the elements under study.

To confirm the oxidation state of platinum metal present in the nanoclusters, the solid was characterized using XPS. Thus, powdered Pt-nanoclusters were deposited (approximately 10 mm height) on carbon-coated aluminum tab and analyzed by XPS. The XPS spectra of Pt-nanoclusters showed two peaks at 72.75 eV [$Pt(4f_{7/2})$] and 75.5 eV [$Pt(4f_{5/2}$] which are in good agreement with reported results of $Pt(4f_{7/2})$ binding energy in Pt-Si bonds and in zero oxidation state of platinum (Figure 6). The existence of Pt-Si

bonds clearly indicates the covalent interaction of polysiloxane matrix with platinum nanoparticles.

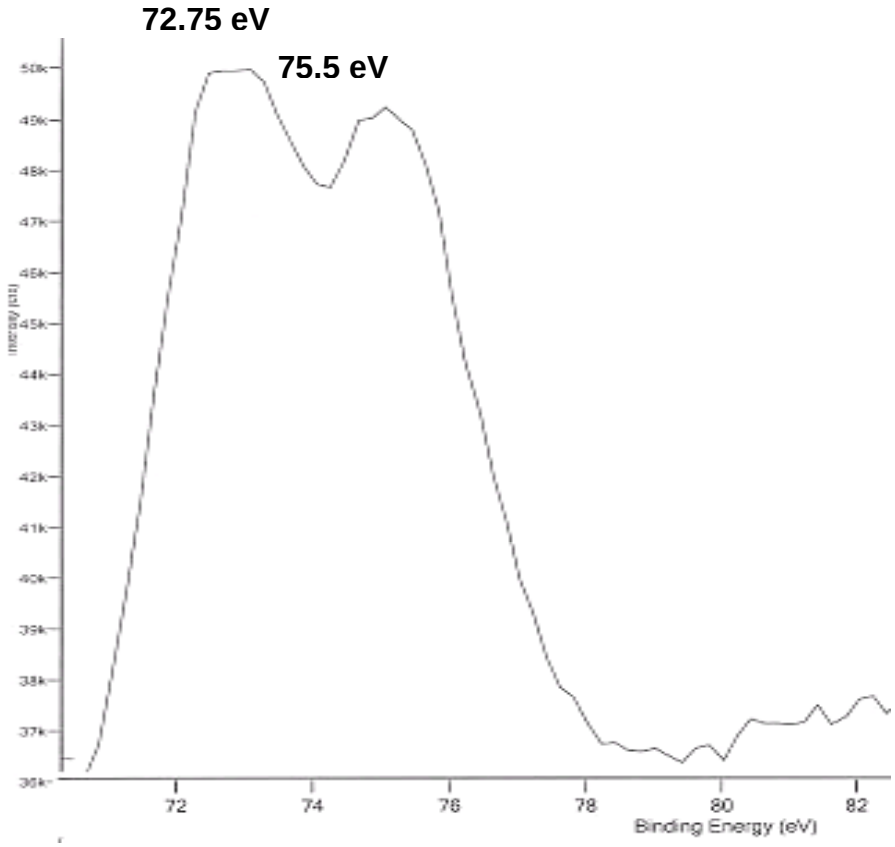


Figure 6. XPS spectra of the Pt-nanoclusters

1.5.3. Characterization of Pt-nanoclusters. Solid State Multinuclear Spectroscopic and UV-vis Characterization of the Solid.

To investigate the status of the siloxane matrix in the solid, sample was analyzed by multinuclear solid-state NMR. The ^{13}C CP/MAS spectra of the solids showed a single broad peak at δ -3.36 corresponding to the methyl groups on the silicon centers (figure 7). Absence of any peak in the olefin regions confirmed complete removal of organic ligand 1,5 cyclooctadiene, which was initially present in the $Me_2Pt(COD)$. The solid-state ^{29}Si NMR spectra displayed four peaks (δ -107.86, -75.30, -68.70, and –35.0) indicating the

presence of Q (bonded to four oxygen), T (bonded to three oxygen) and Si-H silicon centers (Figure 8). Presence of the Q, T, and Si-H silicon centers were also observed with FT-IR spectra of the solid, which showed peaks at ν (cm^{-1}) = 2175 (Si-H), 1120 (Si-O-R), 1050 (Si-O-Si), 893 (Si-OH). The solid state UV-vis spectra of the Pt-nanoclusters showed a featureless spectra ruling out any possibility of Pt-complex formation by a reverse reactions (Figure 9).

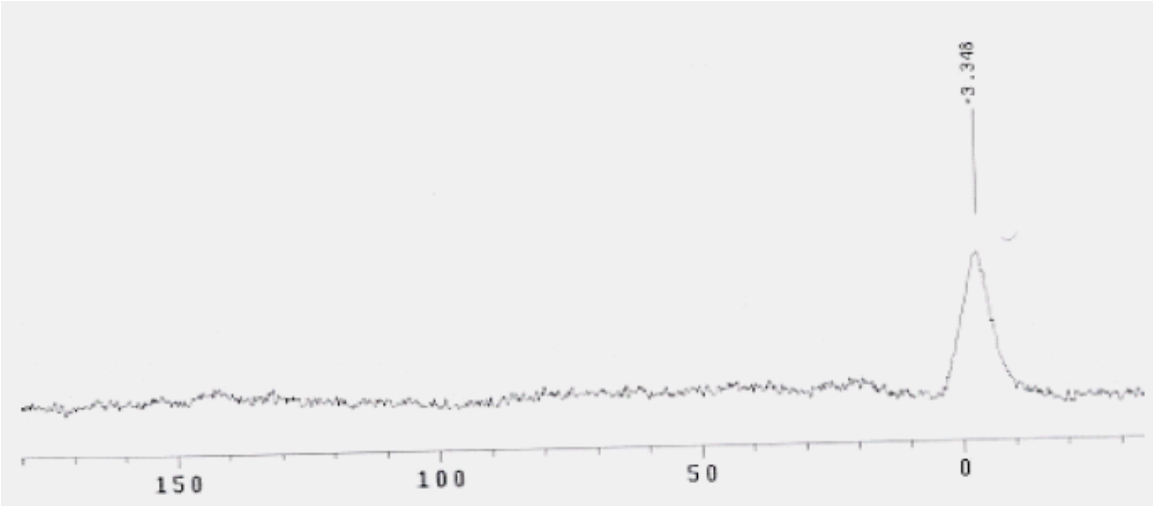


Figure 7: CP/MAS ^{13}C spectra of the Pt-nanoclusters.

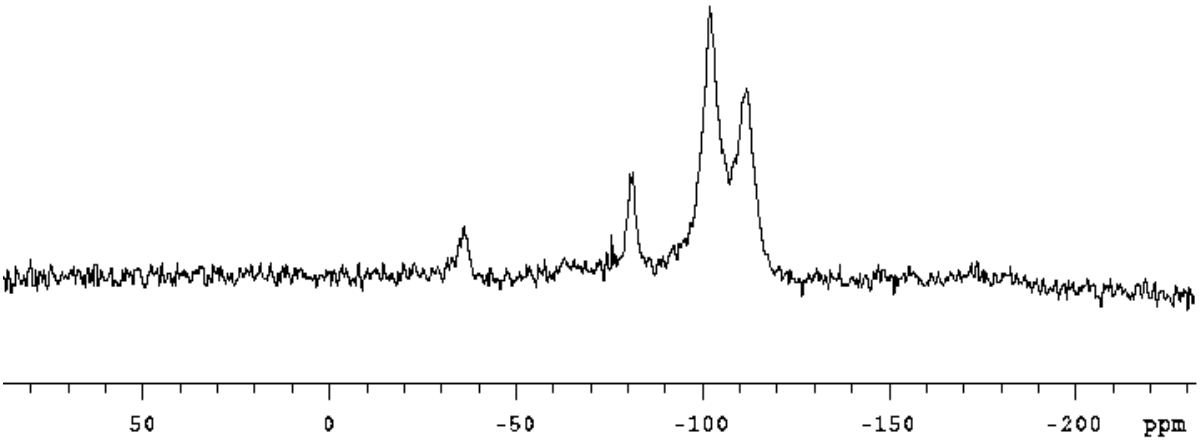


Figure 8: ^{29}Si NMR spectra of the Pt-nanoclusters.

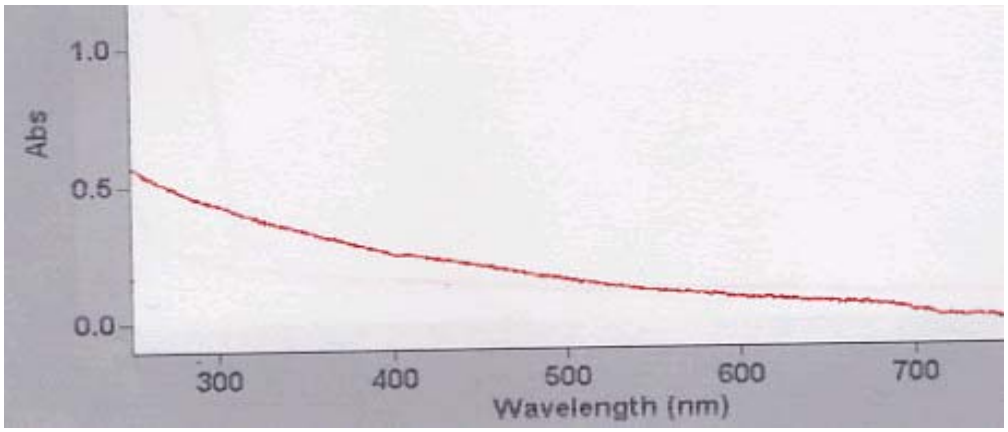


Figure 9: Solid state UV-Vis spectra of Pt-nanoclusters

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Chapter 2

Functional Vinylsilanes and Vinylgermanes via Pt-nanocluster Catalyzed Selective addition of E-H (E=Si, Ge) to alkynes

2.1. Vinylsilanes

Vinylmetallic species are useful building blocks in various organic reactions.[1] Among various vinylorganometallics, vinylsilanes particularly attracted increasing attention due to their ease of handling, low cost, low toxicity and simplicity in removal of byproduct. There is plethora of literature where vinylsilanes has been used in various important roles. For example (i) nucleophilic partners in the palladium catalyzed cross-coupling reactions,[2] (ii) acceptor in conjugate addition reactions, (iii) masked ketones in Tamao-Fleming oxidation,[3] and (iv) terminator for cationic cyclizations.[4] Well-defined bis(vinylsilane)s also find applications in polymer chemistry as precursors for the synthesis of silylene-spaced conjugated polymers.[5]

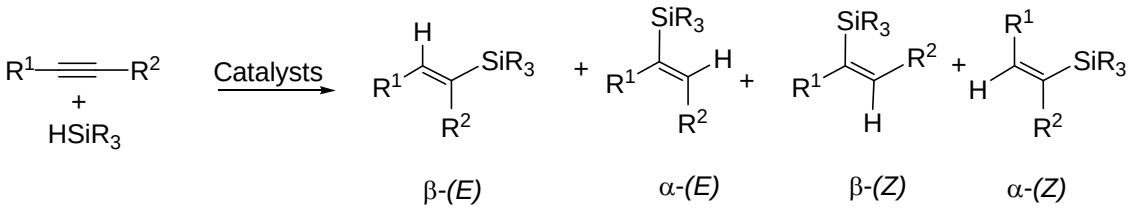
Hydrosilylation across the carbon-carbon triple bonds is one of the simplest, atom economic and efficient method for the synthesis of vinylsilanes. Since the discovery of catalytic hydrosilylation of unsaturated carbon bonds using chloroplatinic acid by J.L. Speier in 1957,[6] there have been many studies of catalysis of hydrosilylation by transition metal complexes. Some of the important transition metals, which have been involved in this study, are Pt, Rh, Co, Ru, Pd, and Ni.[7] Although a wide range of catalysts has been studied for hydrosilylation, most of the industrial research has been involved with the Pt complex, H_2PtCl_6. In recent years, Karstedt's catalyst,[7e] obtained by treating hexachloroplatinic acid with vinyl siloxane, has been the most used catalyst.

Over the past few decades, the issue of selectivity in the hydrosilylation reaction of alkynes has been studied extensively using various transition metals including Ru, Rh, Pt, Ir, Ti-based complexes and Lewis acid as catalysts. Generally, the hydrosilylation of alkynes can produce four possible products: the β-(*E*), α-(*E*), β-(*Z*) and α-(*Z*)(Scheme 1).

The product distribution found to vary depending upon the nature of the catalyst and substrates.

Platinum metal complexes are well-established catalysts for hydrosilylation reaction. Hydrosilylation of alkynes in presence of platinum catalysts generally leads to syn-addition of silanes across the triple bond of alkyne affording a mixture of α(*E*) and β(*E*) isomers.[8] However it has been studied in the past that by tuning the ligands, the product regioselectivity can be improved.[9] The [Cp*Ru]-based catalysts most often gave α-isomers,[4] while the zero valent rhodium and iridium complexes afforded β-isomers predominantly.[5] A titanocene-based complexes (such as Cp_2TiCl_2) have also been reported as alkyne hydrosilylation catalysts giving rise to syn-addition products predominantly.[10] Although a significant improvement in selectivity has been achieved using Lewis acid catalysts;[11] poor yields and formation of non-hydrosilylated byproducts impeded the widespread applicability of such catalysis.

Scheme 1. Distribution of products in the hydrosilylation reaction of alkyne.



Recyclability of the catalyst is another important issue from the standpoint of atom economy and simplicity of product purification. Most of the metal-complex catalysts are homogenous in nature and often require specialty ligands for stereo- or regioselective transformations. Removal of such toxic metals and ligands from the organic product is quite difficult and requires additional effort. Moreover, the metal-complex catalysts are often highly expensive. Therefore, the recyclability of the catalyst

becomes one of the most desirable properties of the catalyst in terms of both synthetic and commercial applications. The recyclability can be achieved by using a biphasic reaction conditions or other immobilization systems.

The immobilization of hexachloroplatinic acid and other metal catalysts has become one of the focus areas of the organosilicon chemistry in early 1970s. It was assumed that supported-metal catalysts have the advantages of both homogenous and heterogeneous catalysis. The main advantages of the supported catalysts are as follows (i) the ease of catalyst recovery (ii) high regio- and stereo- selectivity and (iii) ease of handling.[12] For example, polymer-resin supported Speier's catalysts has shown improved catalytic activity by minimizing other isomerization reactions during the hydrosilylation of alkenes compared the homogeneous Speier's catalyst. Also, the catalyst has shown long term recyclability with minimum quantity of platinum leaching.[13] In related work, K_2PtCl_4 immobilized on microporous polystyrene-based resins has also shown improved activity by minimizing the isomerization of 1-octene during hydrosilylation reactions compared to homogeneous K_2PtCl_4 catalyst.[14] Recently, $Pt(PPh_3)_4$ has been immobilized using polymer incarcerated method, which has shown comparable catalytic activity to that of homogenous platinum complexes, along with added advantage of recyclability.[15] In a recent report, the catalytic activity of silica-supported platinum (Pt/SiO_2) towards hydrosilylation of mono- and disubstituted alkynes has been investigated. The studies have revealed the possibility of controlling the stereochemistry of the hydrosilylation product by changing the nature of phase of the heterogeous systems. [16] Recently, ionic liquids have been recognized as potential means for the immobilization of catalysts. However, the number of reports on the considered hydrosilylation reactions in ionic

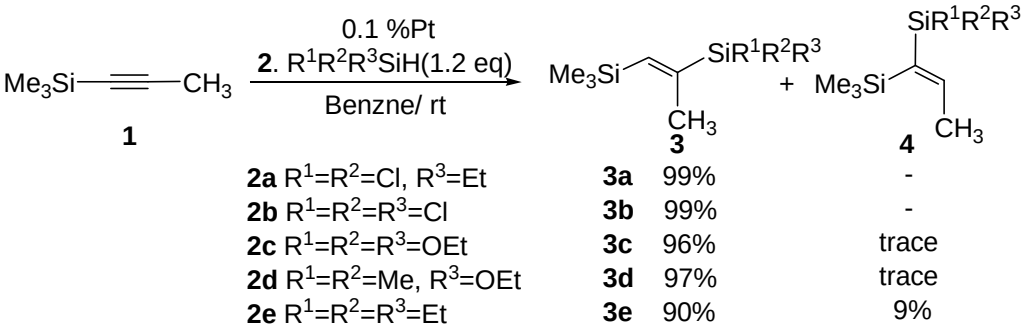
liquids is quite limited. Notable examples include rhodium-catalyzed biphasic hydrosilylation of ketones, enones, alkenes and alkynes.[17]

Recently, our group has demonstrated the macromolecular grafting of PMHS via polysiloxane-stabilized Pt-nanoclusters catalyzed regio-selective olefin-hydrosilylation reactions.[18] The catalyst has shown promising activity with respect to the efficiency, selectivity, ease of product purification, and recyclability. In this chapter, we describe a highly regio- and stereo- selective hydrosilylation and hydrogermylation of functional alkynes via Pt-nanoclusters catalysis. In addition, investigation of true nature of catalyst during the catalysis has also been described.

2.1.2. Pt-nanocluster-Catalyzed Hydrosilylation of Alkynes

The catalytic activity and selectivity of polysiloxane stabilized Pt-nanoclusters for the hydrosilylation reaction of various functional alkynes have been studied. In a preliminary experiment, a schlenk tube was charged with Pt-nanocluster (0.005 g, 0.001 mmol of Pt) and flushed with nitrogen. Dry benzene (2 mL) and trimethylsilyl-1-propyne **1** (0.138 gm, 1 mmol) were added consecutively. To this suspension, ethyldichlorosilane **2a** (0.14 mL, 1.2 mmol) was added and the mixture was allowed to stir continuously at room temperature (Scheme 3).

Scheme 2: Polysiloxane-stabilized Pt-nanocluster-catalyzed hydrosilylation of disubstituted acetylene.



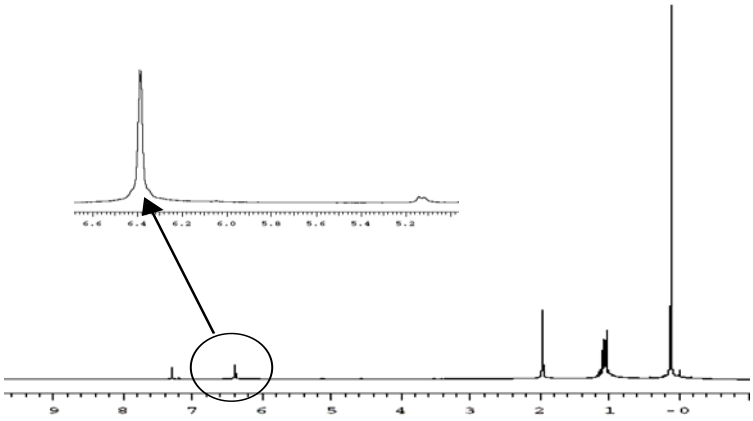
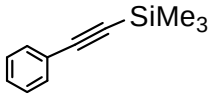
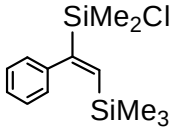
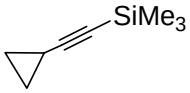
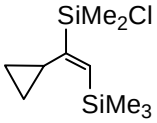
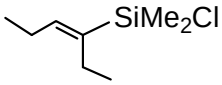
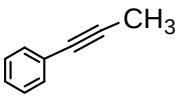
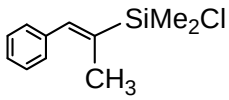
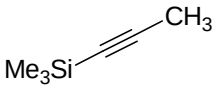
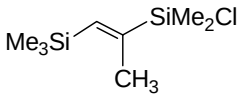


Figure 1. The ^{1}HNMR of the crude reaction mixture (entry 1, scheme 2)

After 10 minutes of the reaction, the color of the solution turned light yellow with gradual dispersion of the catalyst. The reaction mixture was monitored by ^{1}HNMR, which indicated quantitative conversion of alkyne to corresponding hydrosilylated product **3a** after 10h of reaction (figure 1). Product isolation was simply carried out by centrifugation of the reaction mixture followed by solvent evaporation. Detailed NMR analysis indicated exclusive formation product **3a** with no detectable amount of any other isomers. [19] The reaction of alkyne **1** was examined in presence of silanes **2b-2d** (Scheme 2) under identical conditions and afforded **3b**, **3c** and **3d** with high stereo and regioselectivity. Only trace of other regio isomer (0-3%) was observed. However, in case of triethylsilane comparatively lower (Scheme 1; **3e**: **4e**= 91: 9) selectivity was observed.

As an important functional group, dimethylchlorosilane can offer easy access to various organic transformations.[20] So in order to extend the scope of the reaction, further investigation was carried out using dimethylchlorosilane with a variety of disubstituted acetylenes. Excellent yields (> 95%) and selectivity (> 97 %) were achieved for the entire range of alkyne substrates (Table 1). The hydrosilylation of phenyltrimethylsilylacetylene (entry A) and phenylmethylacetylene (entry D), which have been reported as very sluggish and less selective with other catalyst, [19d] smoothly proceeded in presence of dimethylchlorosilane to afford corresponding hydrosilylated product(s) with high regio and stereo-selectivities. The hydrosilylation of cyclopropyl-substituted acetylene (entry B) was achieved without any interruption of the ring, to afford selective formation of single product. When a symmetrical alkyne, 3-hexyne (entry C) was employed for the hydrosilylation reaction, only one isomer was furnished.

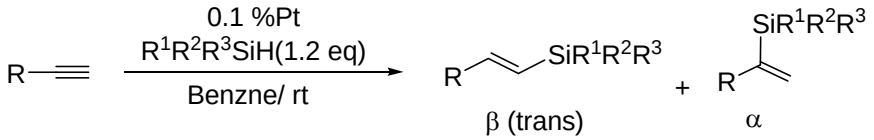
Table 1: Polysiloxane-stabilized Pt-nanocluster-Catalyzed hydrosilylation of disubstituted acetylene with $HSiMe_2Cl$. [a]

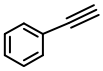
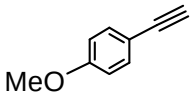
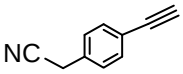
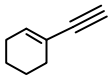
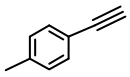
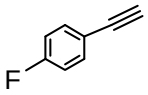
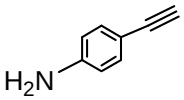
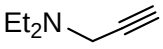
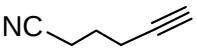
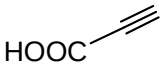
Ent.	Alkyne	Major Product	Yield % [b] major: minor
A			98[c] (97: trace)
B			98[c](98: trace)
C			98 (na)
D			98[c] (92: 08)
E			95 (98: trace)

[a]Conditions: [Alkyne]= 1.0 mmol; [silane]=1.5 mmol; Pt-nanocluster = (0.001 mmol); At Room Temperature, [b]Yield refer to isolated pure product(s). [c]Required longer reaction period (24h) and addition of excess of silane (3 equiv).

Terminal acetylenes were also examined for hydrosilylation reaction using various silanes. The reaction is quite general affording trans disubstituted vinylsilanes (85-97 %) with a trace quantity (3-15%) of corresponding α-product (Table 2). Formation of β- (trans) and α-isomer were inferred from the typical vinyl (J =18-20 Hz) and geminal (J =4-6 Hz) proton-proton coupling in ^{1}HNMR. No cis-isomer was obtained during the hydrosilylation reaction. The reaction is tolerant of wide variety of functional groups (Table 2) such as internal olefin, amine, cyano, halide and methoxy.

Table 2. Pt-nanocluster-catalyzed hydrosilylation of terminal acetylenes .[a]



Entry	Alkyne	Silane	Time (h)	Yield % (β-trans: α)[c]
1		$HSiMe_2Cl$	10	96(98: 02)
2		$HSiMe_2Cl$	10	92(96: 04)
3		$HSiMe_2Cl$	16	92(88: 12)
4		$HSiMe_2Cl$	16	94(97: 03)
5		$HSiEt_3$	10	96(86: 14)
6		$HSiEt_3$	10	95(85: 15)
7		$HSiEt_3$	10[b]	94(88: 12)
8		$HSiEt_3$	20[b]	96(92: 08)
9		$HSiEt_3$	20[b]	95(87: 13)
10		$HSiEt_3$	20[b]	95(40: 60)

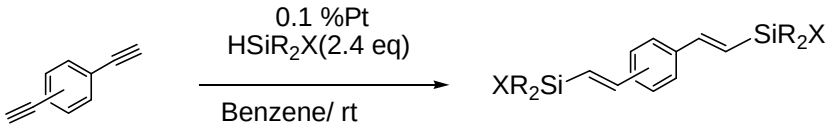
[a]Conditions: [Alkyne]= 1.0 mmol; [silane]=1.2 mmol; Pt-nanocluster = (0.001 mmol); and Room Temperature, Solvent: Benzene, [b]at 70^0C. [c]Yields are based on isolated products.

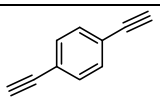
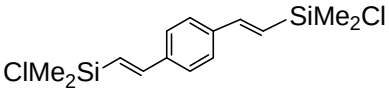
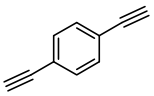
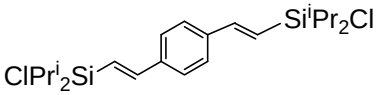
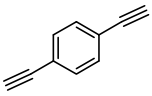
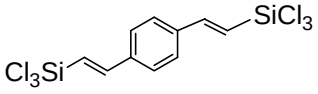
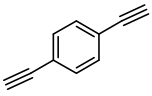
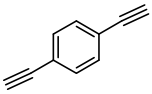
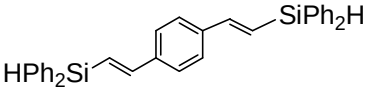
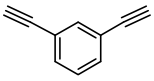
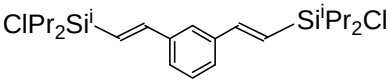
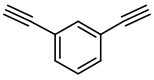
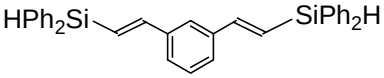
Recently silylene-spaced conjugated polymers are receiving increasing interest because of their interesting blue light emitting property.[21] Moreover; introduction of

silicon moiety into the polymer backbone has shown significant improvement in the solubility of the polymers. Though hydrosilylation provides useful source of such polymers, due to the limited accessibility of silane monomers, the syntheses are normally limited to alkynyl silyl hydrides for their use as starting materials. Recently, Luh and coworkers have reported synthesis of silylene-spaced divinylarene copolymers via hydrosilylation of bisalkynes with bisvinylsilanes, where the bisvinylsilanes were prepared using a four-step method.[22] However, for easy access to a variety of bisvinylsilanes, a general synthetic development would be highly desirable. Although, there has been significant progress in transition metal catalyzed hydrosilylation to provide mono-vinylsilanes, only a limited reports is known about the synthesis of bisvinylsilanes.

To determine the scope of the present catalytic approach in the hydrosilylation of bisalkynes, the hydrosilylation of various bis(ethynyl)benzenes was examined using variety of chlorosilanes (Table 3 & 4). The chlorosilanes were purposefully chosen because the synthesized chloro-products can easily be converted to corresponding bisvinylhydrosilanes through $LiAlH_4$ reductions. A variety of silanes smoothly underwent hydrosilylation with bis(ethynyl)benzenes in highly regio and stereo selective fashion to afford only one isomer, except in case of di-t-butylsilane where no reaction was observed with substituted alkynes (entry 4, table 4) and a mixture of products was obtained with terminal alkynes (entry 4, table 3).

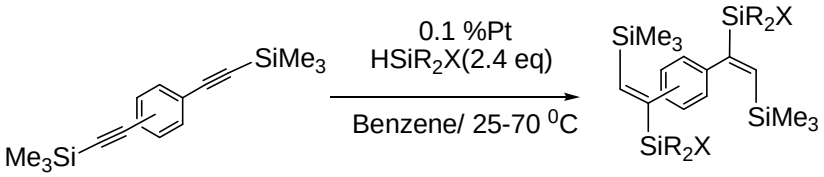
Table 3. Pt-nanocluster-catalyzed hydrosilylation of terminal bis(ethynyl)benzenes

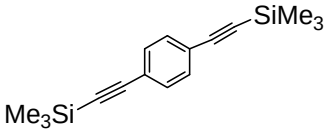
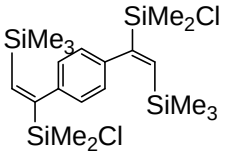
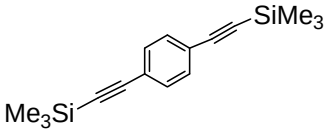
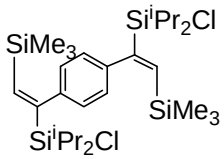
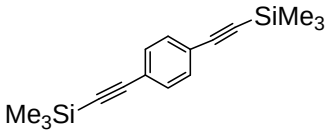
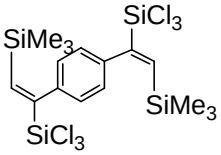
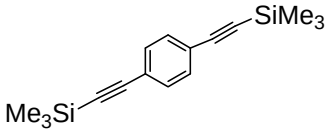
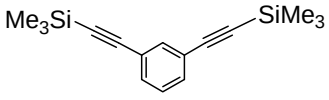
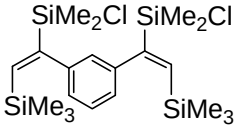
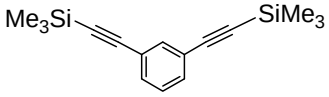
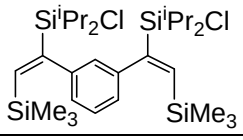


Ent.	Alkyne	Silane	Time/h	Product	Yield[c]
1		$HSiMe_2Cl$	10h		98
2		$HSiPr^i_2Cl$	10h[b]		96
3		$HSiCl_3$	24h		98
4		$H_2SiBu^t_2$	24h[b]	A mixture of α and β isomers	nd
5		H_2SiPh_2	24h[b]		96
6		$HSiPr^i_2Cl$	10h[b]		98
7		H_2SiPh_2	24h[b]		95

[a]Conditions: [Alkyne]= 1.0 mmol; [silane]=2.5 mmol; Pt-nanocluster = (0.001 mmol); and Room Temperature, Solvent: Benzene, [b]at 70^0C. [c]Yields are based on isolated products.

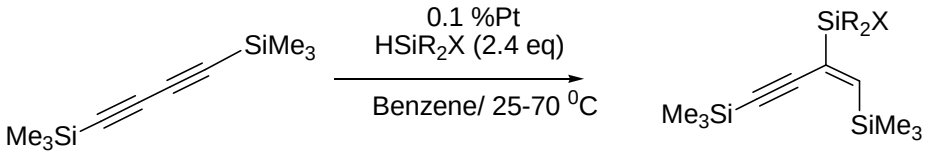
Table 4. Pt-nanocluster-catalyzed hydrosilylation of trimethylsilyl-substituted bis(ethynyl)benzenes

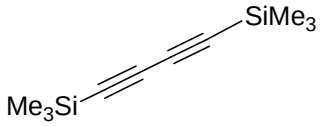
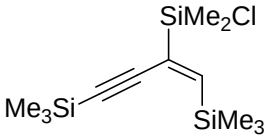
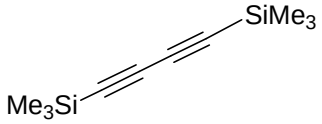
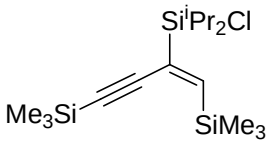
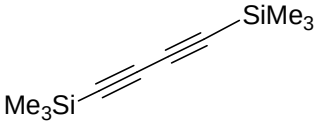
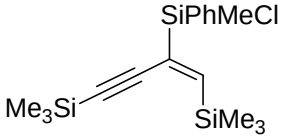
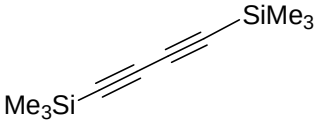
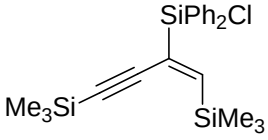
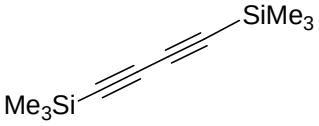
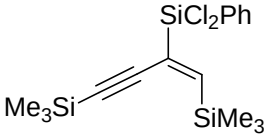


Ent.	Alkyne	Silane	Product	Yield[c]
1		$HSiMe_2Cl$		98
2		$HSiPr^i_2Cl$[b]		96
3		$HSiCl_3$		95
4		H_2SiPh_2[b]	No Reaction	na
5		$HSiMe_2Cl$		98
6		$HSiPr^i_2Cl$[b]		98

[a]Conditions: [Alkyne]= 1.0 mmol; [silane]=2.5 mmol; Pt-nanocluster = 0.005g (0.001 mmol), [Time]=24h; and Room Temperature, Solvent: Benzene, [b]at 70^0C. [c]Yields are based on isolated products.

Table 5. Pt-nanocluster-catalyzed hydrosilylation of bis(trimethylsilyl)-1,3-butadiyne.



Ent.	Alkyne	Silane	Product	Yield[c]
1		$HSiMe_2Cl$		98
2		$HSiPr^i_2Cl$[b]		98
3		$HSiPhMeCl$[b]		96
4		$HSiPh_2Cl$[b]		98
5		$HSiMe_2Cl$		98

[a]Conditions: [Alkyne]= 1.0 mmol; [silane]=1.2 mmol; Pt-nanocluster = 0.005g (0.001 mmol), [Time]=24h; and Room Temperature, Solvent: Benzene, [b]at 70^0C. [c]Yields are based on isolated products.

A series of terminal and trimethylsilyl-substituted bisalkynes were employed for the hydrosilylation reaction. The terminal bis(ethynyl)benzenes underwent hydrosilylation to afford the product with complete β-(*E*) selectivity, whereas the hydrosilylation of trimethylsilyl-substituted bis(ethynyl)benzenes afforded α-(*E*) isomer quantitatively. The hydrosilylation of trimethylsilyl-substituted 1,3-butadiyne afforded a single product originating from the selective hydrosilylation of one of the two triple

bonds (Table 5). Also, it is to our surprise that even at higher concentration of silanes the second triple bond does not undergo further hydrosilylation. The high selectivity of this reaction achieved through our methodology is one of the interesting aspects of our catalysis. In general, the hydrosilylation of alkynes shows dramatic differences in product distribution depending upon the nature of the substrate and the catalysts. All the products were thoroughly characterized using ^{1}H, ^{13}C and ^{29}Si NMR techniques. The β-(*E*) configuration was verified by the characteristic large coupling constant of the vinylic protons (*J*=18.6-19.2 Hz), whereas the α-(*E*) configuration of the product was verified based upon the X-ray crystallographic analysis of one of the representative products (Figure 2). The crystallographic data and processing parameters are given in Table 6.

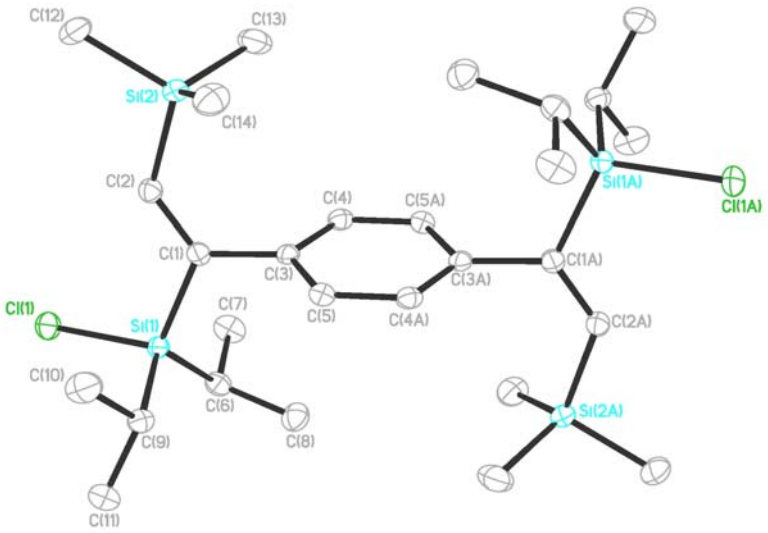


Figure 2. Single Crystal X-ray of 1, 4-Bis{(*E*)-α-diisopropylchlorosilyl-β-trimethylsilylethenyl}benzene (entry 2, table 4)

Table 6. Crystal Data and Structure Refinement for 1,4-Bis{(*E*)-α-diisopropylchlorosilyl-β-trimethylsilylethenyl}benzene (entry 2, table 4)[a]

Empirical formula	$C_{28}H_{52}Cl_2Si_4$	
Formula weight	571.96	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.5248(5) Å	α= 90°.
	B = 15.5373(9) Å	β= 104.3430(10)°.
	C = 13.1884(8) Å	γ = 90°.
Volume	1692.39(17) $Å^3$	
Z	2	
Density (calculated)	1.122 Mg/m^3	
Absorption coefficient	0.349 mm^{-1}	
F(000)	620	
Crystal size	0.32 x 0.23 x 0.15 mm^3	
Theta range for data collection	2.06 to 27.50°.	
Index ranges	-11<=h<=10, -20<=k<=16, -16<=l<=14	
Reflections collected	10213	
Independent reflections	3742 [R(int) = 0.0233]	
Completeness to theta = 27.50°	96.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.825	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3742 / 0 / 258	
Goodness-of-fit on F^2	1.165	
Final R indices [I>2sigma(I)]	R1 = 0.0366, wR2 = 0.0886	
R indices (all data)	R1 = 0.0394, wR2 = 0.0901	
Largest diff. Peak and hole	0.487 and -0.184 $e.Å^{-3}$	

[a]We are thankful to Prof. A. L. Rheingold at UCSD for helping with X-ray analysis.

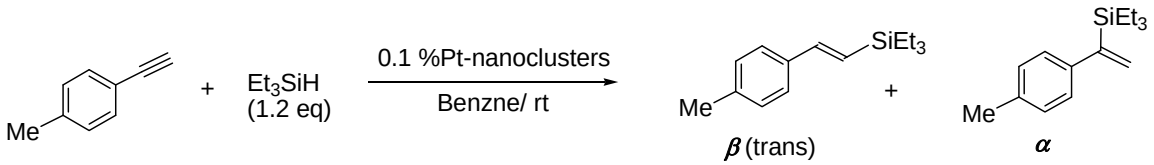
2.1.3. Investigation of the Nature of the Catalysis

Identification of the true nature of the catalysts during the transition-metal catalysis has caused considerable challenges due to potential involvement of molecular-level catalytic species. In the past few decades, a number of publications have appeared describing various approaches to distinguish nanoclusters catalysis from homogenous metal-complex catalysis.[23] Recently, Finke and co-workers outlined a thorough and more general approach for distinguishing the nanocluster catalysis from single metal-complex catalysis.[24] Based on Finke's approach, we performed the following experiments to establish the true nature of the catalyst; (a) TEM and UV-vis studies during the catalysis, (b) Quantitative poisoning studies, (c) Generation of the nanoclusters in presence of poisoning agents and their characterization studies, and (d) Catalyst isolation and recyclability experiments.

(a) TEM and UV-vis Studies. UV-vis spectroscopy is one of the most common and widely used techniques for nanoparticle characterization. Certain metal nanoparticles such as silver, gold, and copper show a series of plasmon bands depending upon the size and shapes of the nanoparticle,[25] while other metals e.g. Pd, Pt, and Ni show featureless spectrum. Moreover, UV-vis spectral technique can also help in detecting the in-situ generated metal complexes, which can act as real catalysts. In our study, the Pt-nanoclusters have a featureless UV-vis spectra whereas its precursor, $Me_2Pt(COD)$ shows a UV-absorption peak at ~320 nm. Also, a well-dispersed solution of Pt-nanoclusters shows the presence of Pt-nanoparticles in the TEM experiments. In our preliminary studies of investigating true nature of the catalyst, we have utilized TEM and UV-vis techniques. We have conducted a hydrosilylation reaction of ethynyl toluene using

triethylsilane and Pt-nanoclusters as catalyst (scheme 3). During the catalysis (after 2h) one drop of crude reaction mixture was deposited on formvar/carbon-coated copper grid and analyzed by TEM, which showed the presence of Pt-nanoparticle in the size regime of 1-2 nm (Figure 3).

Scheme 3: Polysiloxane-stabilized Pt-nanocluster-catalyzed hydrosilylation of 1-ethynyltoluene with triethylsilane.



The reaction was also monitored by UV-visible spectroscopy by taking an aliquots (1.0 mL) of the reaction mixture at regular intervals of time (0.5 h, 2.5 h and 10 h). A featureless spectrum, which is a characteristic feature of Pt-nanoclusters, was obtained throughout the course of the catalysis (Figure 4).

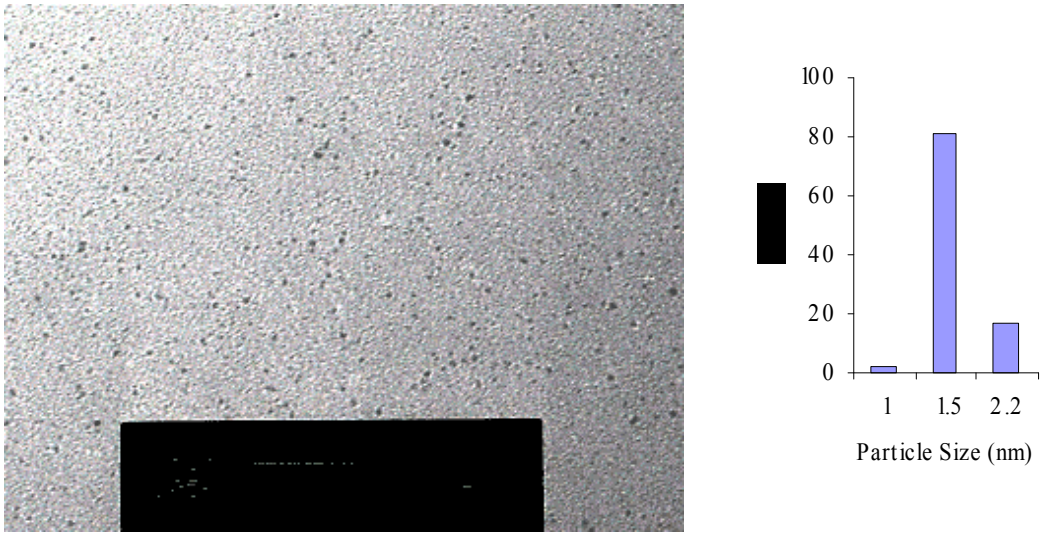


Figure 3. TEM image of Pt-nanoclusters during the reaction (scale bar =50 nm)

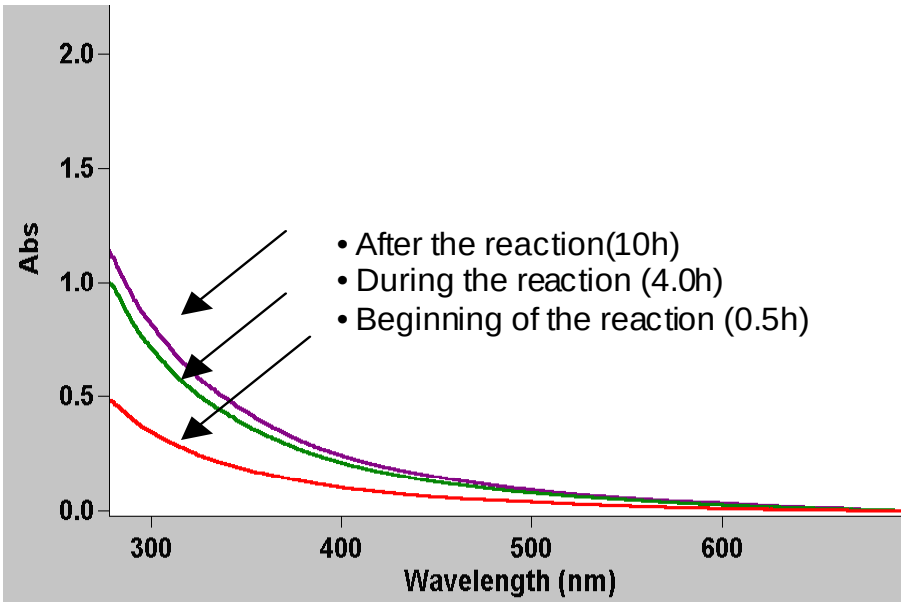


Figure 4. UV-Vis spectra of Pt-nanocluster-catalyzed hydrosilylation at different time interval.

(b) Poisoning Studies. The coordinating ligands such as dodecanethiol (DDT), PPh_3, CS_2 and thiophene can strongly passivate the surface of the nanoparticles, making the nanoparticles catalytically inactive.[24] Therefore, study of catalytic activity of Pt-nanoclusters in presence of such ligands would provide us some information about the nature of the present catalysis, i.e. if only the nanoparticles are involved in the catalysis, the catalysis must be inhibited in presence of such poisoning ligands.

The poisoning studies were performed using ligands, dodecanethiol (DDT), triphenylphosphine (PPh_3) and pyridine. In a typical procedure, the hydrosilylation reaction 4-ethynyltoluene with triethylsilane was performed in three different Schlenk tubes in presence of different amounts of DDT (0.0005 mmol, 0.001 mmol and 0.002 mmol) (scheme 4). The reaction mixtures were monitored using ^1H NMR; while we observed a significant retardation of catalysis with 0.5 and 1.0 equivalent of DDT (0.0005

mmol and 0.001 mmol) and complete retardation was observed with 2.0 equivalent of DDT (0.002 mmol) (table 7). The identical results were also observed with other coordinating ligands such as PPh_3 and pyridine (table 8 and table 9). It has been observed that there was no significant change in the selectivity of the reactions in presence of different poisoning agents. An additional poisoning experiment was performed by adding DDT (0.002 mmol) after ~40 % conversion of the reaction; no reaction was observed thereafter (figure 5); even though Pt-nanoparticles were still present (Figure 5).

Scheme 4: Polysiloxane-stabilized Pt-nanoclusters catalyzed hydrosilylation of 4-ethynyltoluene with triethylsilane in presence of poisoning agents.

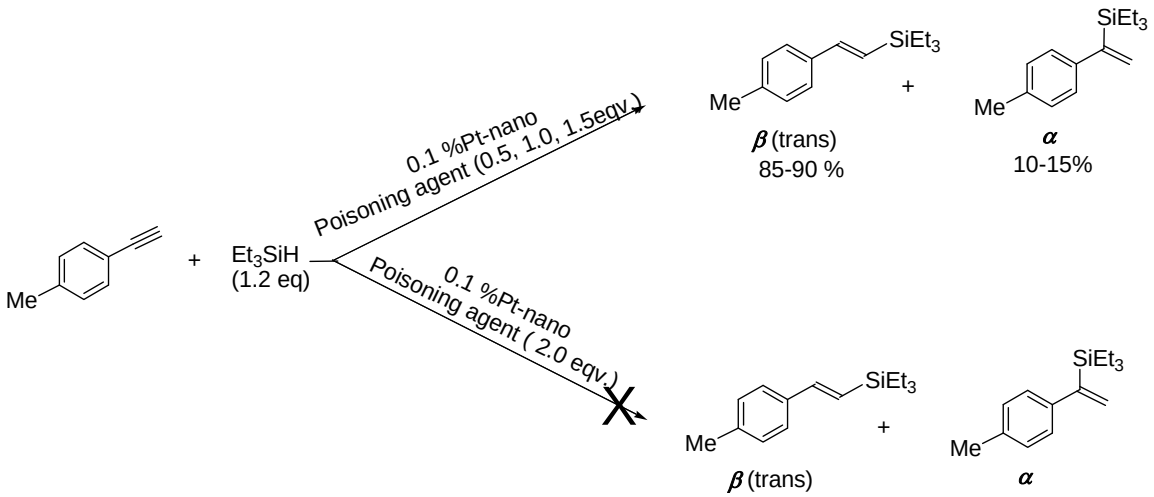


Table 7: Hydrosilylation of 4-ethynylbenzene in presence of DDT.

Time (h)	% Conversion (0.5 equiv of DDT)	% Conversion (1.0 equiv of DDT)	% Conversion (2.0 equiv of DDT)
1	12	5	0
5	18	9	0
24	35	17	0

Table 8: Hydrosilylation of 4-ethynylbenzene in presence of PPh_3.

Time (h)	% Conversion (0.5 equiv of PPh3)	% Conversion (1.0 equiv of PPh3)	% Conversion (2.0 equiv of PPh_3)
1	7	4	0
5	13	7	0
24	26	13	0

Table 9: Hydrosilylation of 4-ethynylbenzene in presence of pyridine.

Time (h)	% Conversion (0.5 equiv of pyridine)	% Conversion (1.0 equiv of pyridine)	% Conversion (2.0 equiv of pyridine)
1	8	5	0
5	10	7	0
24	30	19	0

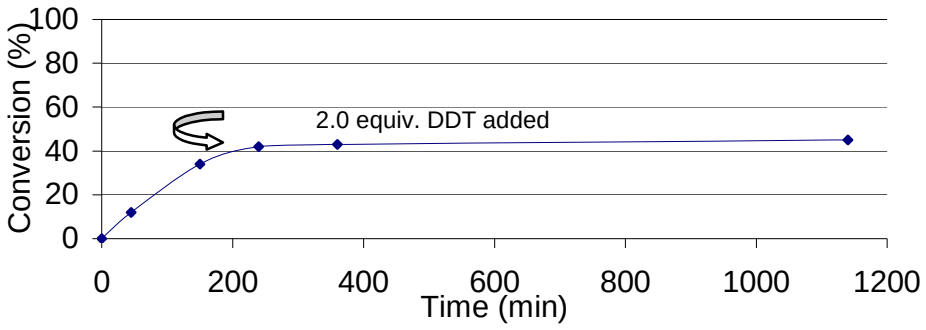


Figure 5. Catalyst poisoning during the catalysis using DDT.

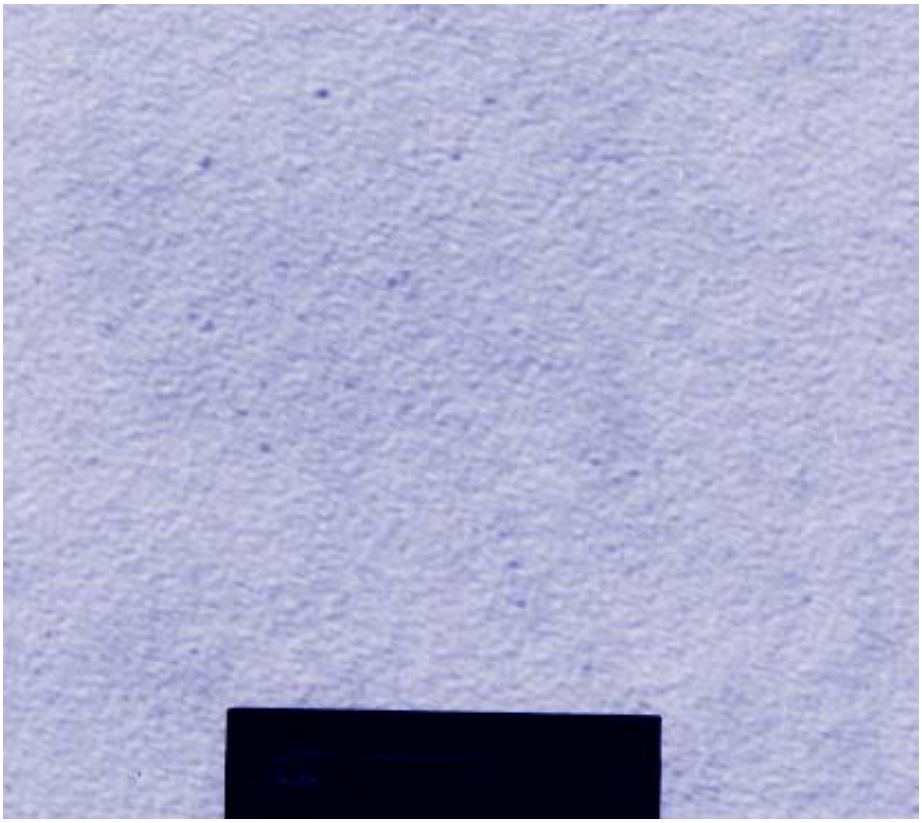


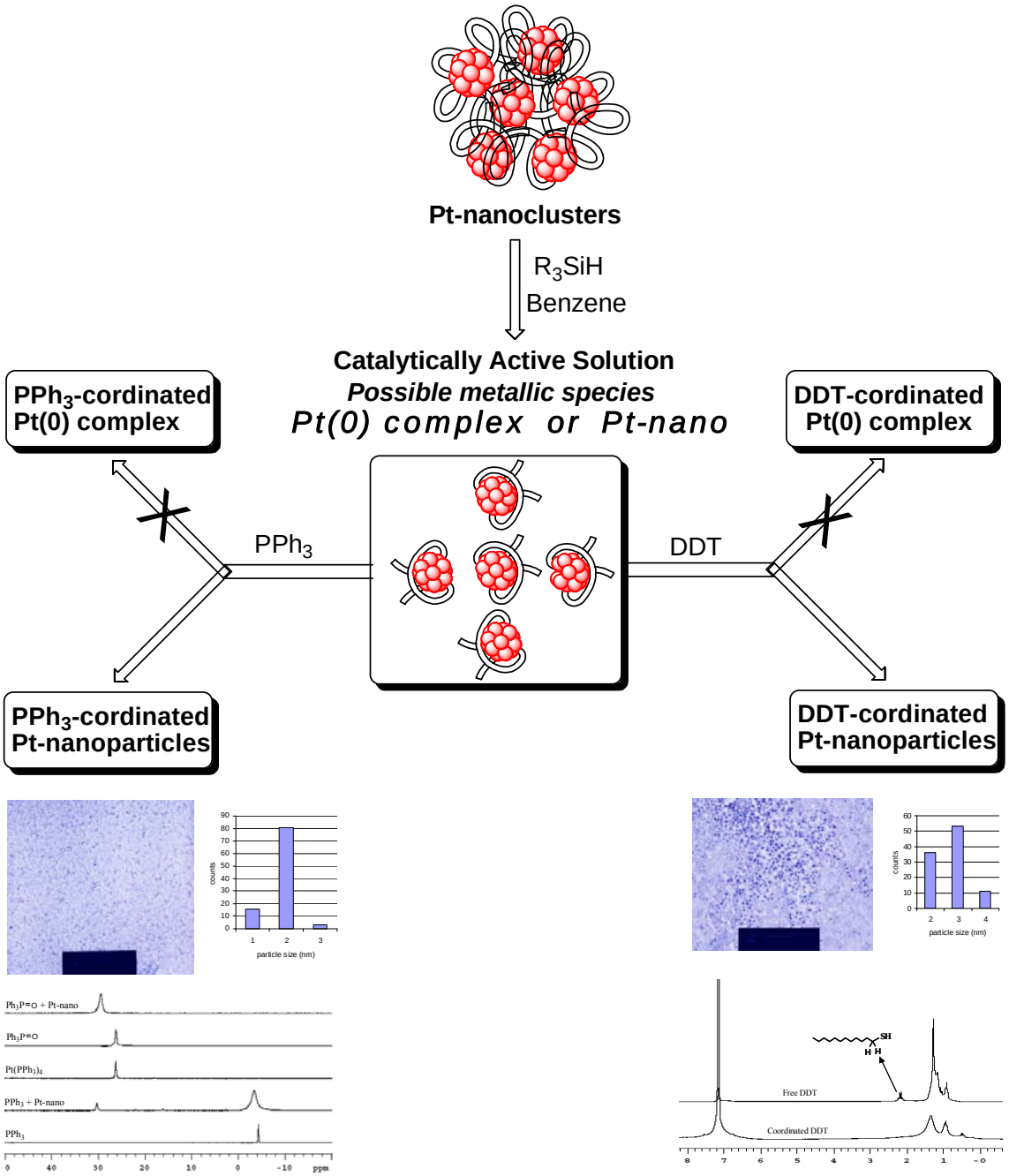
Figure 5. TEM image of the reaction mixture in presence of DDT (scale bar = 20 nm).

(c) Generation of the nanoclusters in presence of the poisoning agents and their characterization. In the presence of a strong coordinating ligand, there is a possibility of disassembling of metal nanoparticles into monometallic complex (eq. 1),[24] due to which it becomes very difficult to distinguish between metal particle catalysis and monometallic catalysis.

$$M_n + (x.n)L \longrightarrow nML_x$$ **(Eq. 1. Adapted after Ref 24)**

To study the nature of the Pt-nanoclusters in presence of such coordinating ligands, Pt-nanoclusters were dispersed in presence of DDT or PPh_3 and analyzed the samples using NMR spectroscopy (Scheme 5). As nanoparticle-bound ligands will show their own characteristic signals in the NMR spectroscopy, it is easier to recognize the formation of any monometallic complex with the corresponding ligand.[26]

Scheme 5. Strategy to distinguish nanoparticle catalysis from monometallic complex catalysis.



In an experimental procedure, a schlenk tube was charged with Pt-nanoclusters (0.01 mmol, 0.05 g) and benzene-d_6 (1 mL) under the flow of nitrogen. To this

suspension, DDT (0.02 mmol, 4.7 μL) was added and the reaction mixture was allowed to stir under nitrogen at room temperature for 24 h. After centrifugation, a dark homogenous solution was obtained which was analyzed by ^{1}H NMR and TEM. The NMR spectrum were correlated to those reported for the dodecanethiol stabilized Pt-nanoparticles, indicating the thiolate attachment to the platinum metal core (Figure 6).[26] The same solution was analyzed by TEM, which showed the presence of nanoparticles, in the size regime of 2-3 nm (Figure 7). The catalytic activity of these thiol stabilized Pt-nanoclusters was also tested using our standard reaction conditions (entry 5, Table 2), and no significant catalytic activity was observed even after 48h.

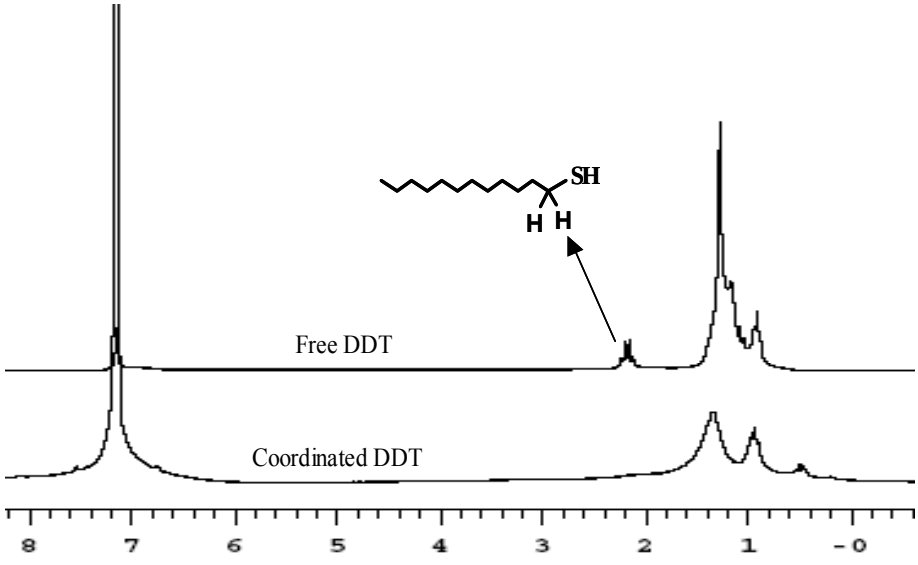


Figure 6. The stacked NMR spectra of free DDT and coordinated DDT.

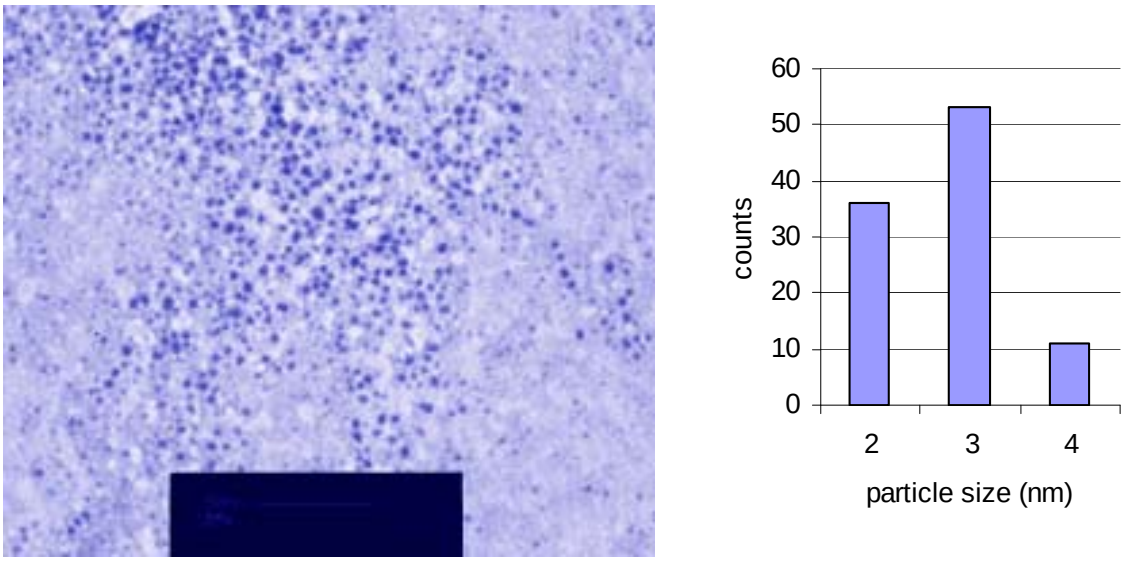


Figure 7. TEM analysis of DDT-stabilized Pt-nanoclusters.

In another experiment, an attempt was made to prepare PPh_3 stabilized Pt-nanoparticles under the identical procedure described above. The schlenk tube was charged with Pt-nanoclusters (0.01 mmol, 0.05 g), PPh_3 (0.02 mmol, 0.005 g). To this mixture, benezene-d_6 (1.0 mL) and, triethylsilane (1.0 mmol, 0.112 mL) was added and the resulting mixture was stirred at room temperature for 24 h. After 30 minutes, the color of the solution became dark-brown with the gradual dispersion of Pt-nanoclusters. After centrifugation, a light yellow solution was obtained which was analyzed by TEM and ^{31}P NMR. The attachment of the phosphine ligand to the nanoparticle was clearly indicated by broadening of the ^{31}P NMR peak (δ=-3.5 ppm) and also by slight change in the chemical shift from δ=-4.5 ppm (free phosphine) to δ=-3.5 ppm (Figure 8). An additional peak corresponding to the nanoparticle-bound triphenylphosphine oxide ($Ph_3P=O$) was also observed at $\delta \approx 30.0$. The triphenylphosphine oxide could possibly be generated because of the oxidation of triphenylphosphine. No formation of monometallic Pt-complex, such as tetrakis(triphenylphosphine) [$Pt(PPh_3)_4$] was observed even after the

addition of excess triphenylphosphine (10.0 eqv.) as indicated by NMR spectroscopy (Figure 9). The TEM analysis of these solutions revealed the presence of spherical Pt-nanoparticles in the size regime of 1.0- 2.0 nm (Figure 10).

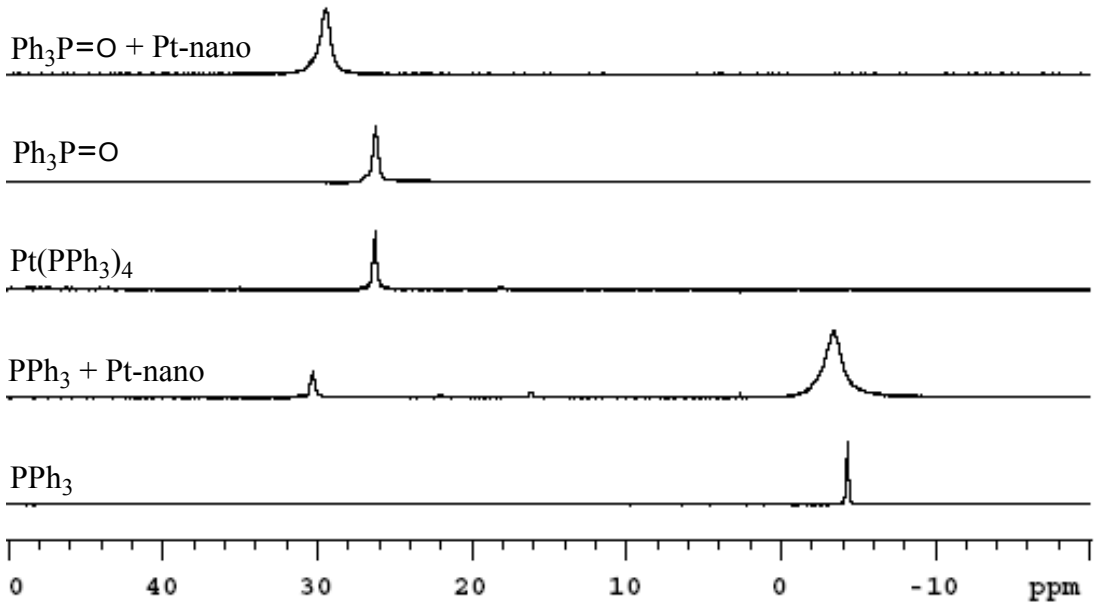


Figure 8. The stacked ^{31}PNMR Spectra of free, coordinated and complexed PPh_3.

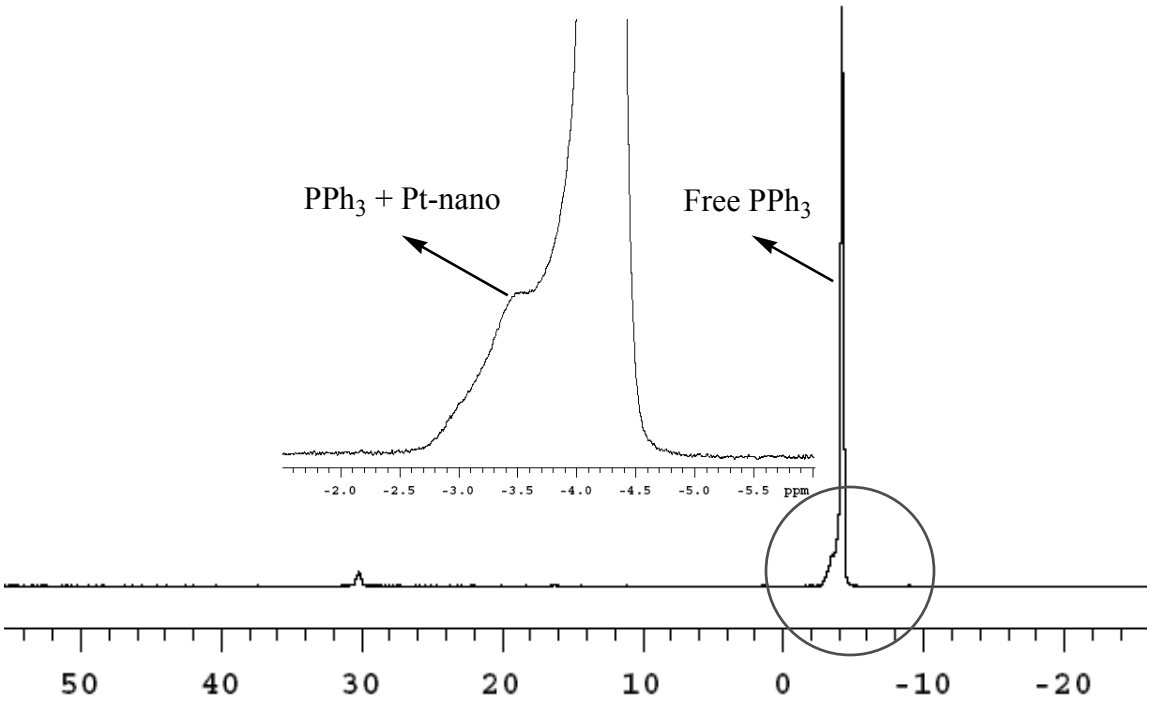


Figure 9. The ^{31}PNMR spectra of free, coordinated PPh_3 (inset: magnification of the highlighted portion).

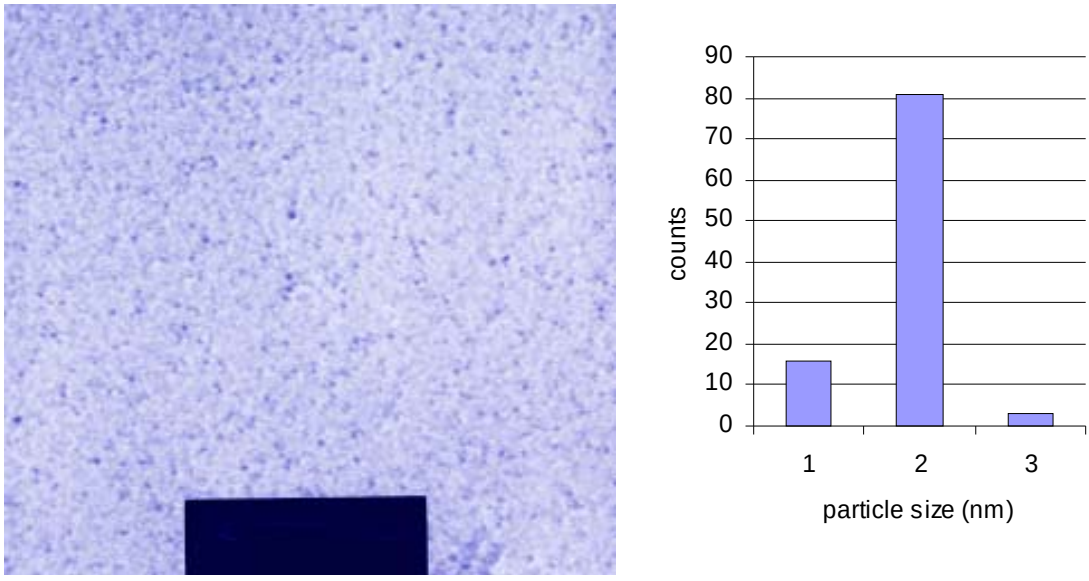
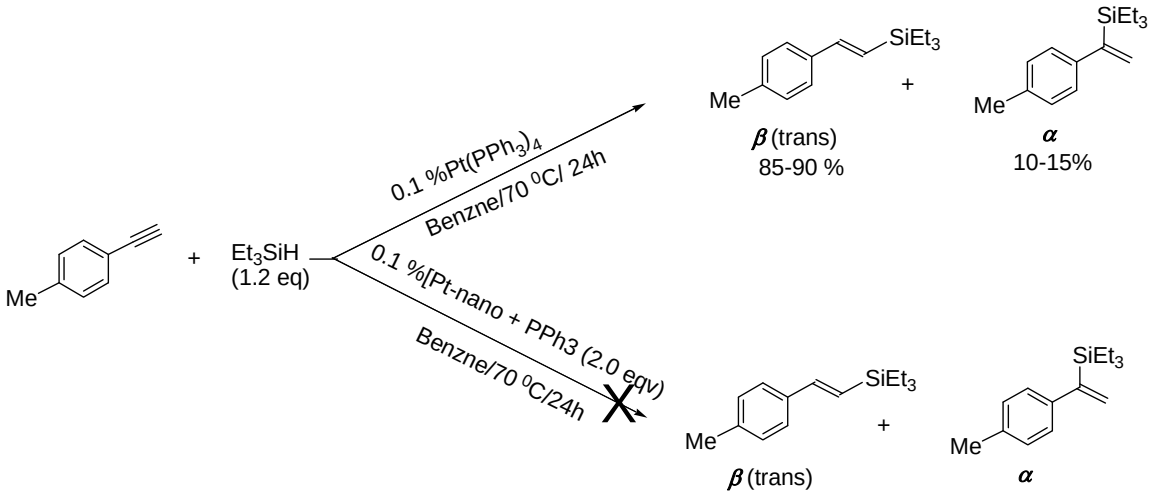


Figure 10. TEM analysis of PPh_3 stabilized Pt-nanoclusters.

To further distinguish the present nanoclusters catalysis from a homogenous metal complex catalysis, the catalytic activity of PPh_3-coordinated Pt-nanoclusters was

examined and compared with that of $Pt(PPh_3)_4$ complex. The hydrosilylation of 1-ethynyltoluene smoothly underwent in presence of the complex $Pt(PPh_3)_4$ at 70 ^{0}C, where as no significant catalytic activity was observed with PPh_3-coordinated Pt-nanoclusters [Pt-nanoclusters + PPh_3-(2.0 eqv)] (Scheme 6). This proves that the present catalysis does not involve in the formation of any monometallic Pt-complex.

Scheme 6: Hydrosilylation of 4-ethynyltoluene in the presence of $Pt(PPh_3)_4$ and PPh_3-Pt-nanoclusters conjugate.



In conclusion, we have proved in both the experiments that there was no possibility of formation of monometallic species during the catalysis, which in turn proves the true nature of catalysis as "nano-particle catalysis"

(d) Catalyst Isolation and Recyclability Studies. Isolation and recyclability of the catalysts is one of the important characteristic features of metal nanocluster catalysis. Isolation of the nanoclusters using the centrifugation techniques has been known for many years.[24] To test the recycling property of the present catalysts, the catalyst was isolated from the crude reaction mixture by simple centrifugation technique and reused

for several cycles. Thus, a Schlenk tube was charged with Pt-nanoclusters (0.005 g, 0.0001 mmol) benzene-d_6 (2 mL), 4-ethynyltoluene (0.13 mL, 1.0 mmol) and triethylsilane (0.19 mL, 1.2 mmol). The mixture was stirred at room temperature. After the completion of reaction (10 h) as monitored by ^{1}H NMR spectroscopy, the catalyst was separated by high-speed centrifugation (20 min) technique and thoroughly washed with dry benzene. The washed catalyst was dried under vacuum and reused for 5 additional cycles. Consistent catalytic activity was observed for 5 reaction cycles with complete conversion of reactants in 10 hours. The catalytic activity was found to decrease from 6th cycle onwards, with only 87% of conversion in 10 hours of reaction time.

2.2. Functional Vinylgermanes via Pt-nanocluster Catalysis

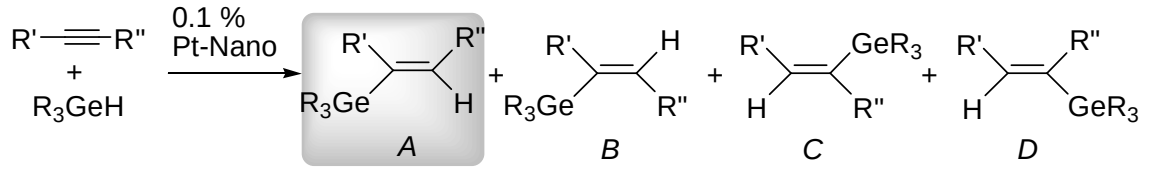
Functional vinylgermanes have application in organic synthesis and materials chemistry, but synthetic routes to such synthones have not been fully explored.[27] Metal catalyzed hydrogermylation of multiple bonds, therefore, represents a useful class of catalytic processes, which can produce such synthones, but very limited number of reports has appeared in literature.[28] The major consideration in this conversion is selectivity, the control of which although highly desirable, is not an easy task in most cases. For example, in limited examples available, most of the reactions afford mixture of possible isomers and are carried out with activated hydrogermanes or alkynes. To the best of our knowledge, systematic studies of nano-sized metal catalyzed hydrogermylation reactions of functional alkynes are not known.

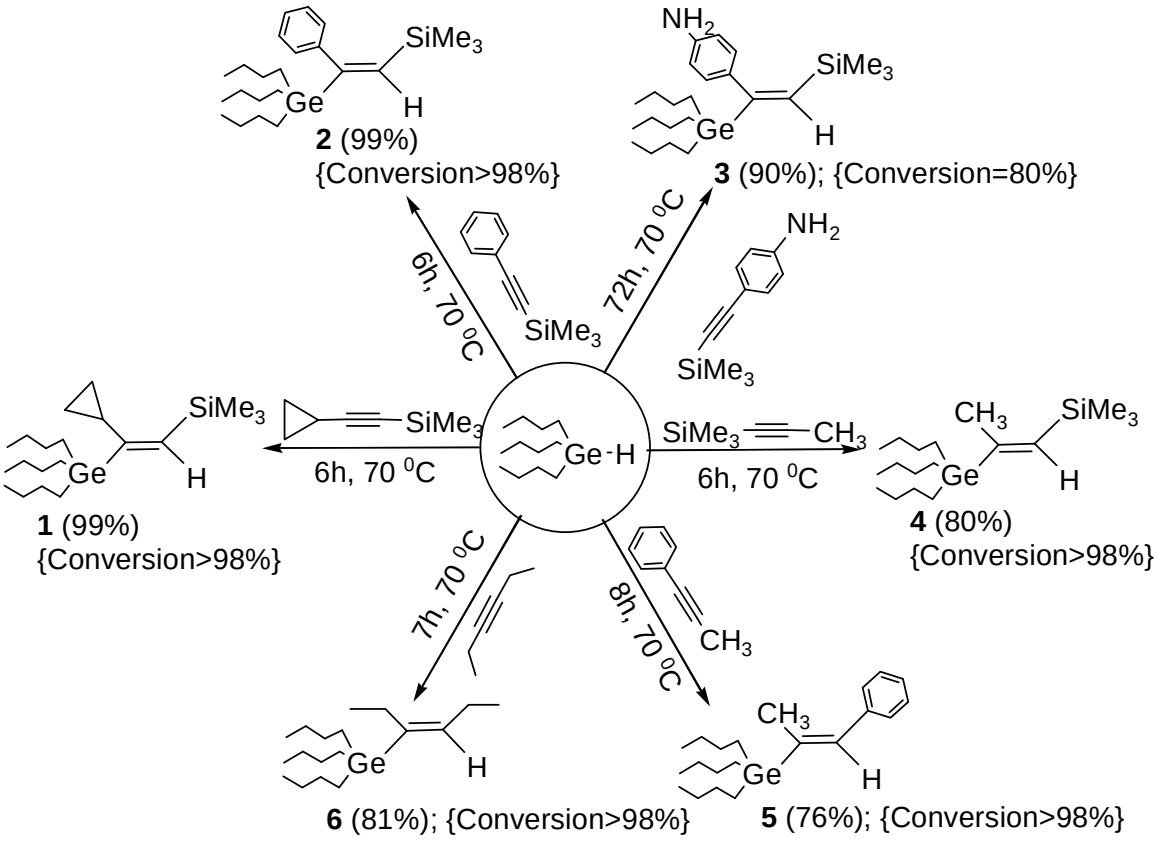
Here, we describe first example of Pt-nanocluster-catalyzed, mild, one pot, high yield, stereoselective hydrogermylation of functional alkynes. In addition, we also

present preliminary studies of the nature of recyclable nanocluster catalysts during the catalysis.

The catalytic activity and selectivity of polysiloxane stabilized Pt-nanoclusters for the hydrogermylation reaction of cyclopropyl(trimethylsilyl) acetylene was examined using tri-n-butylgermane. A Schlenk tube was charged with Pt-nanocluster (0.005 g, 0.001 mmol of Pt) and flushed with nitrogen. To this solid catalyst, dry benzene and cyclopropyl (trimethylsilyl) acetylene (0.138 g, 1.0 mmol) were added followed by tri-n-butylgermane (0.267 mL. 1.0 mmol). After a few minutes, the color of the solution turned light yellow with gradual dispersion of the catalyst into the reaction mixture. The reaction mixture was monitored by NMR, which indicated complete conversion of starting materials after 6 h of the reaction. The catalyst was separated by centrifugation. Detailed analysis of this liquid showed selective (98%) formation of product **1** (isomer type A) from four possible isomers (Scheme 7). The stereochemistry of product **1** was determined by studying nuclear Overhauser effect (nOe) in the ^{1}H NMR.

Scheme 7: Pt-nanocluster-catalyzed hydrogermylation of disubstituted alkynes.





The control of regio- and stereoselectivity of hydrogermylation of alkynes is a very difficult task and generalization of such a process is even more challenging. In view of the synthetic utility of such a selective transformation, studies were carried out with a series of disubstituted alkynes (Scheme 6). The relative proportion of the products was determined by careful integration of the vinylic resonances in the ^{1}H-NMR spectrum. To our surprise, alkynes substituted with trimethylsilyl group afforded exclusively or predominantly one isomer, in which tri-n-butylgermanium group was attached trans to

trimethysilyl group. The reaction was found to be quite general and applicable to both aromatic and aliphatic acetylenes In all the cases except for **3**, quantitative conversion to corresponding vinyl germanes was observed. Even generally less reactive symmetrical disubstituted alkynes, such as 3-hexyne reacted cleanly to furnish desired hydrogermylation product in quantitative yield. The catalytic transformation also takes place at room temperature though longer time periods (≈ 24h) were required. In all cases, formation of isomer type **C** was also observed ranging from trace amounts up to 16% .

To investigate the scope and limitations of present catalysis, a series of functional terminal alkynes were also investigated (Scheme 8). The results are summarized in the table 10. The hydrogermylation of unsymmetrical terminal alkynes can give rise to three different products via addition of germanium at either end of triple bond (Scheme 6).[27] To our surprise, in the absence of strongly polar neighboring substituents, the reactions were highly selective and gave predominantly the isomer in which germanium is bound to the less substituted carbon atom (anti-Markovnikov addition).

Scheme 8: Hydrogermylation of terminal acetylenes using Pt-nanoclusters catalyst.

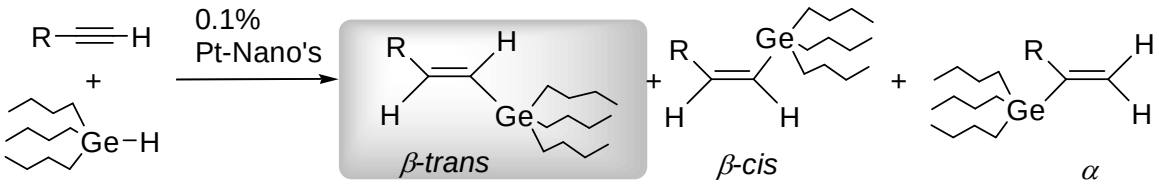
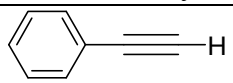
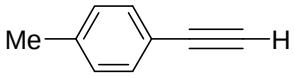
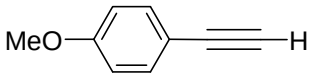
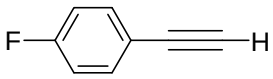
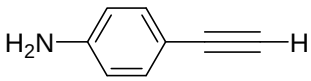
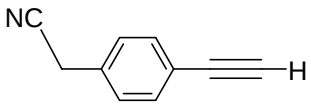
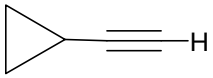
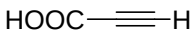
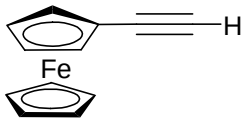


Table 10. Pt-nanocluster-catalyzed selective hydrogermylation of terminal alkynes.

Entry	Monosubstituted Alkyne	Reaction Conditions[b]	% Yields [c] (β–trans:α)
1		6h/70 ^{0}C	99 (85:15)
2		6h/70 ^{0}C	97 (88:12)
3		8h/70 ^{0}C	95 (82:18)
4		6h/70 ^{0}C	98 (78:22)
5		6h/70 ^{0}C	98 (95:05)
6		8h/70 ^{0}C	98 (89:11)
7		6h/RT	98 (91:09)
8		6h/70 ^{0}C	96 (44:56)
9		6h/70 ^{0}C	98 (94:06)

[a]Molar Ratio's: [Alkyne]= 1 mmol; [(n-C_4H_9)$_3$GeH]= 1 mmol; Pt-Nanocluster = (0.005 g); [b]Solvent: Benzene; [c]Yields based on ^{1}H NMR.

The directive effect of polar substituents strongly influences the product proportions of the hydrogermylation reactions of monosubstituted alkynes. In case of phenyl acetylenes, we found a variation in β-selectivity (anti-Markovnikov addition), depending on the electronic nature of the substituents present on the *p*-position of the phenyl group. The

ratio of α-product formation increases with the electro-negativity of the substituents on phenyl group, (Table 10, entry 1-4).

In case of hydrogermylation of cyclopropylacetylene (Table 10, entry 7) exclusively β-trans product was obtained. However, acid-containing acetylene (Table 10, entry 8) led to mixture of α, β products. It is noteworthy that the nanocluster catalysis was tolerant of variety of functional groups providing a direct access to functional vinyl germanes.

2.2.1. Investigations of the Nature of True Catalyst

To investigate the nature of catalyst we performed following experiments during the catalysis: (1) TEM and UV-vis studies of the precursors and their transformation to catalytically active nanoclusters; (2) quantitative poisoning studies and (3) recyclability and reproducibility studies.

(a) TEM and UV-vis Studies During the Catalysis. In a typical experiment, Pt-nanoclusters composite (0.005 g, 0.001 mmol) was suspended in dry benzene (3 mL) and phenylacetylene (0.109 mL, 1 mmol) was added. To this mixture tri-n-butylgermane (0.267 mL, 1 mmol) was added. After few minutes the mixture turned homogeneous with gradual dispersion of the catalyst into the reaction mixture. The reaction mixture was monitored by NMR, UV-vis and Transmission Electron Microscopy (TEM) techniques during the catalysis. ^{1}H-NMR analysis of the crude reaction mixture after an interval of ~1 h showed ~50% hydrogermylation of alkyne moiety. At this juncture, one drop of the reaction mixture was directly deposited on formvar/carbon coated grid and analyzed by TEM (Figure 11), which showed the presence of dispersed Pt-nanoparticles in ~2 nm size range. Additionally, UV-vis analysis of the reaction mixture was performed at regular

intervals and showed featureless spectra, a characteristic of Pt-nanoclusters (Figure 12) No other UV-vis peak was observed during the transformation or after the termination of the reaction.

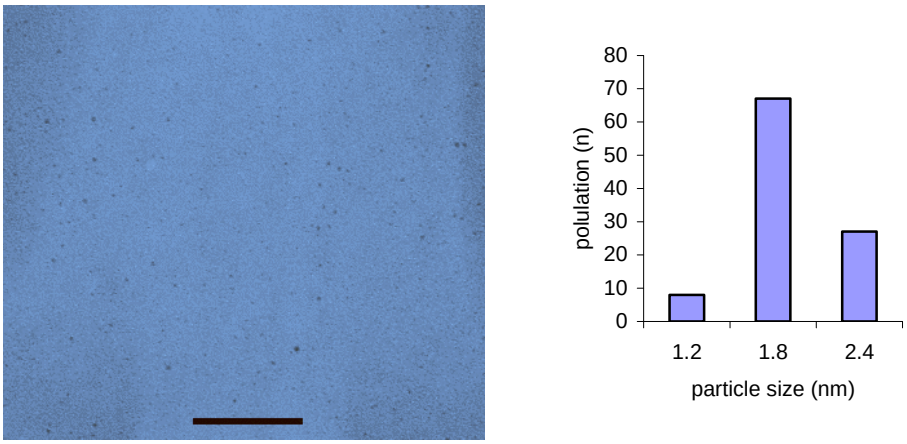


Figure 11. TEM image and particle size analysis

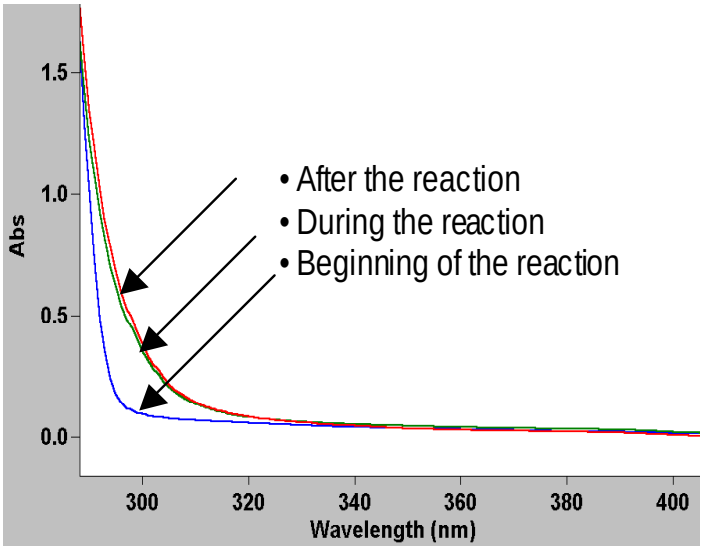


Figure 12. UV-vis analysis during the catalysis

(b) Catalyst Poisoning Studies. Metal-particle catalysts have an exaggerated sensitivity to poisons because only a fraction of the metal atoms are expected to be on the surface of the particle and active. Poisoning experiment using added ligands such as PPh_3 is an important tool for the investigation of nanocluster catalysis; this is because

triphenylphosphine ligand binds strongly to metal surface, thereby blocking the access of substrate to the active site. To investigate the present nanoclusters catalysis, poisoning experiments have been performed using triphenylphosphine. Three different Schlenk tubes were charged with Pt-nanoclusters (0.005 g, 0.001 mmol) and triphenylphosphine in different molar ratios of 0-0.2 mmol (table 11) under flow of nitrogen. To this solid mixture, dry benzene-d_6 (2 mL) and cyclopropyl(trimethylsilyl)acetylene (0.138 g, 1 mmol) were added under constant stirring. To this reaction mixture *tri-n*-butylgermane (0.267 mL, 1 mmol) was added and continued to stir at 70 ^{0}C. The reactions were monitored by NMR spectroscopy at different time intervals. It has been observed that in presence of PPh_3 (1.0 mmol) the catalytic activity was significantly hindered and with 2.0 equivalents of PPh_3 no catalytic activity was observed.

Table 11. Controlled poisoning experiment of the Pt-nanoclusters catalysis.

Experiment number	Conc. of PPh_3 (eqv.)	Conversion (%)		
		50 min.	90 min.	340 min.
1	0.00	63	76	99
2	1.0	0	7	17
3	2.0	0	0	10

(c) Recyclability Studies. In a typical procedure, Pt-nanoclusters (0.005 g, 0.001 mmol Pt), dry benzene-d_6 (2 mL), cyclopropylacetylene (0.08 mL, 1.0 mmol) and *tri-n*-butylgermane (0.267 mL, 1.0 mmol) were added in a 50-mL Schlenk-tube and stirred at room temperature. After verifying the total consumption of *tri-n*-butylgermane with NMR spectroscopy (7 h), high-speed centrifugation (20 min) of reaction mixture led to precipitation of catalyst. After careful decantation of solution from the centrifuge tube, precipitated catalyst was washed with 5-mL of freshly distilled and dry benzene followed by recharging with reactants i.e. dry benzene-d_6 (2 mL), cyclopropylacetylene (0.08 mL,

1.0 mmol) and *tri*-*n*-butylgermane (0.267 mL, 1.0 mmol). Above mixture was stirred at room temperature to achieve complete substitution (36 h). Four additional recyclability experiments were performed by repeated washing of same batch of catalyst and by recharging the Schlenk-tube with same amount of reactants. Total substitution of Si-H bonds was achieved during each recyclability experiment within the same time-frame (7 h).

2.3. Conclusion

In this chapter we have demonstrated a mild, efficient and selective catalytic route to functional vinylsilanes via Pt-nanoclusters catalysis. The catalysis is tolerant of the presence of various functional groups including methoxy (-OMe), Cyanide (-CN), fluoride (-F), Amine ($-NH_2$), and carboxylic acids (-COOH) on the alkynes. A series of di-alkynes underwent selective hydrosilylation and hydrogermylation under the present catalysis; therefore, the methodology could serve as one pot, efficient and mild route for the synthesis of regio- and stereo-regular silylene-spaced divinylarenes. In situ analysis of the reaction mixture with various techniques (TEM, UV-vis and poisoning and recyclability experiments) strongly supported the participation Pt-nanocluster as the real catalyst.

2.4. Experimental Section

General Information. All of the experiments and manipulations were performed under a positive pressure of dry argon or nitrogen using standard Schlenk-tube techniques. Solvents were purchased from EM Science (Merck) and distilled over sodium/benzophenone before use. PMHS (Mw ≈ 2000), $Me_2Pt(COD)$ and all of the alkynes, silanes and germanes were purchased from Aldrich Chemical Co., GFS

Chemical Co., Gelest Chemical Co. and used as received. ^{1}H NMR, ^{13}C NMR and ^{29}Si NMR spectra were recorded on 200 MHz and 600 MHz Varian Unity NMR instruments. Spectra were referenced internally to the corresponding solvent shifts. Philips CM 100 transmission electron microscope (TEM) was employed to examine the reaction mixture for the presence of Pt-nanoclusters. Scanning electron microscope Amray 1910 (SEM) was used to analyze solid Pt-nanocluster. The amount of Pt present in the cluster was determined on the basis of SEM and elemental analysis of the solid nanoclusters, which is ~ 0.001 mmol per 0.005 g (5 wt%) of the solid.

General Procedure For Hydrosilylation of Mono-Alkynes.

A Schlenk tube was charged with Pt-nanocluster (0.005 g, 0.001 mmol Pt) and flushed thoroughly with dry nitrogen. To this solid catalyst, dry benzene (2 mL) and alkyne (1 mmol) were added consecutively. To this mixture, silane (1.2 mmol) was added and the reaction was allowed to run under constant stirring. After the completion of the reaction (10-16 h), a clear solution was obtained on centrifugation of the reaction mixture. On evaporation of the solvent, the product was obtained as viscous liquid. Isolation of the product was followed by multinuclear NMR spectroscopic characterization of the product.

General Procedure For Hydrosilylation of Bis-Alkynes.

A schlenk tube was charged with Pt-nanoclusters (0.005 g, 0.001 mmol Pt) and flushed thoroughly with dry nitrogen. To this solid catalyst, dry benzene (2 mL) and alkyne (1 mmol) were added consecutively. To this mixture, silane (2.2 mmol) was added and let the reaction run under constant stirring. After the completion of the reaction (10-16 h), a clear solution was obtained on centrifugation of the reaction mixture. On evaporation of

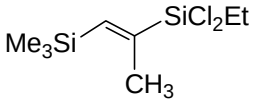
the solvent, the product was obtained as viscous liquid. Isolation of the product was followed by multinuclear NMR spectroscopic characterization of the product.

General Procedure for Hydrogermylation of Alkynes.

A Schlenk tube was charged with Pt-nanoclusters (0.005g, 0.001 mmol Pt) and flushed thoroughly with dry nitrogen. To this solid catalyst, dry benzene (2 mL) and cyclopropyl (trimethylsilyl) acetylene (0.138 g, 1 mmol) were added consecutively. To this reaction mixture tri-n-butylgermane (0.267 mL, 1 mmol) was added under constant stirring. The reaction mixture was placed in an oil bath heated at 70 ^{0}C. After the completion of the reaction (7 h), a clear solution was obtained on centrifugation of the reaction mixture. On evaporation of the solvent the product was obtained as yellowish liquid. Isolation of the product was followed by multinuclear NMR spectroscopic characterization of the product.

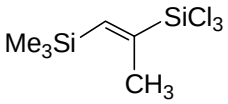
Multinuclear NMR Data of Hydrosilylated Product(s)

(E)-2-(dichloro(ethyl)silyl)-1-(trimethylsilyl)prop-1-ene (entry 2a, Scheme 2)



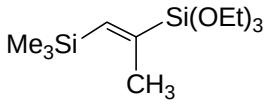
^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.13 (s, 9H), 1.02 (t, 3H, *J*=7.6 Hz), 1.06 (q, 2H, *J*=7.6 Hz), 1.95 (d, 3H, *J*=1.6 Hz), 6.38 (q, 1H, *J*=1.6 Hz). **^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm)-2.7, 6.3, 11.3, 19.3, 148.4, 150.6. **^{29}SiNMR** ($CDCl_3$, 600 MHz): δ (ppm)-9.27, 17.25.

(E)-2-(trichlorosilyl)-1-(trimethylsilyl)prop-1-ene (entry 2b, Scheme 2)



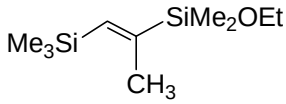
^{1}HNMR ($CDCl_3$, 200 MHz): δ ppm) 0.01 (s, 9H), 1.88 (d, 6H, *J*=1.6 Hz), 6.53 (q, 1H, *J*=1.6 Hz). **^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm) -0.4, 18.5, 147.9, 151.4. **^{29}SiNMR** ($CDCl_3$, 600 MHz): δ (ppm) -8.19, -4.17.

(E)-2-(triethoxysilyl)-1-(trimethylsilyl)prop-1-ene (entry 2c, Scheme 2)



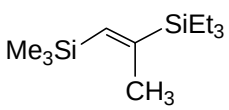
^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.08 (s, 9H), 1.17 (t, 9H, *J*=7.6 Hz), 1.86 (d, 3H, *J*=1.6 Hz), 3.77 (q, 6H, *J*=7.6 Hz), 6.32 (q, 1H, *J*=1.6 Hz). **^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm) -0.1, 18.2, 20.7, 58.5, 147.3, 150.2.

(E)-2-(ethoxydimethylsilyl)-1-(trimethylsilyl)prop-1-ene (entry 2d, scheme 2)



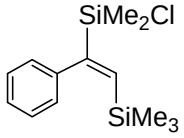
^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) -0.05 (s, 9H), -0.28 (s, 6H), 1.04 (t, 3H, *J*=7.6 Hz), 1.78 (d, 3H, *J*=1.6 Hz), 3.49 (q, 2H, *J*=7.6 Hz), 6.0 (q, 1H, *J*=1.6). **^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm)-2.9, -0.07, 18.3, 20.2, 58.2, 142.7, 157.8. **^{29}SiNMR** ($CDCl_3$, 600 MHz): δ (ppm)-11.31, 5.58.

(E)-2-(triethylsilyl)-1-(trimethylsilyl)prop-1-ene (entry 2e, scheme 2).



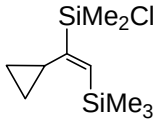
^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.03 (s, 9H), 0.47 (q, 6H, *J*=7.8 Hz), 0.80 (t, 9H, *J*=7.8 Hz), 1.76 (d, 1H, *J*=1.6 Hz), 5.87 (q, 1H, *J*=1.6 Hz). **^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm) 0.3, 1.5, 7.4, 21.7, 142.5, 157.5. **^{29}SiNMR** ($CDCl_3$, 600 MHz): δ (ppm) -11.95, 1.98.

1-((E)-1-(chlorodimethylsilyl)-2-(trimethylsilyl)vinyl)benzene (entry A, Table 1).



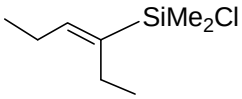
^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) -0.19 (s, 9H), 0.42 (s, 6H), 6.58 (s, 1H), 6.99 (m, 2H,), 7.10 (m, 1H), 7.25 (m, 2H). **^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm) -0.2, 1.3, 126.4, 127.7, 128.8, 142.7, 148.0, 160.8. **^{29}SiNMR** ($CDCl_3$, 600 MHz): δ (ppm) -8.31, 17.05.

((E)-1-(chlorodimethylsilyl)-2-(trimethylsilyl)vinyl)cyclopropane (entry B, Table 1)



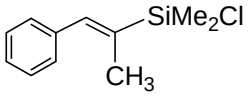
^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.09 (s, 9H), 0.45 (s, 6H), 0.74 (m, 4H), 1.66(m, 1H,), 6.32 (s, 1H).**^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm) 0.0, 3.0, 7.2, 16.9, 147.0, 160.0.

Chloro((E)-hex-3-en-3-yl)dimethylsilane (entry C, Table 1).



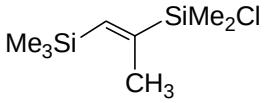
^{1}HNMR ($CDCl_3$, 600 MHz): δ (ppm) 0.37 (s, 6H), 0.89 (t, 3H, *J*=6.6 Hz), 0.90 (t, 3H, *J*=6.6 Hz) 2.05 (dq, 2H, *J*= 6.6 Hz, *J*=6.6 Hz), 2.11(dq, 2H, *J*= 6.6 Hz, *J*=1.6 Hz), 5.80 (tt, 1H, *J*= 6.6 Hz, *J*=1.6 Hz).**^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm) 1.8, 13.7, 14.8, 21.6, 21.7, 138.8, 145.1.

Chlorodimethyl((E)-1-phenylprop-1-en-2-yl)silane (entry D, Table 1).



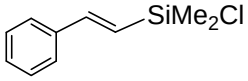
^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.53 (s, 6H), 1.99(d, 3H, *J*=1.6 Hz), 6.88 (q, 1H, *J*=1.6 Hz) 7.20-7.30 (m, 5H). **^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm) 0.9, 15.4, 127.2, 128.2, 129.1, 136.1, 137.1, 139.6. **^{29}SiNMR** ($CDCl_3$, 600 MHz): δ (ppm) 22.07.

(E)-2-(chlorodimethylsilyl)-1-(trimethylsilyl)prop-1-ene (entry E, Table 1).



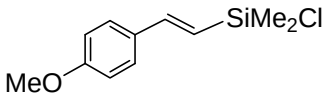
^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.07 (s, 9H), 0.39(s, 6H), 1.89(d, 3H, *J*=1.6 Hz), 6.12 (q, 1H, *J*=1.6 Hz). **^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm) -0.9, 1.0, 19.7, 144.5, 155.3.

Chlorodimethyl(styryl)silane (entry 1, Table 2)



^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.63 (s, 6H), 6.50 (d, 1H, *J*=19.2 Hz) 7.11 (d, 1H, *J*=19.2 Hz), 7.30-7.50 (m, 5H). **^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm) 2.0, 124.5, 126.8, 128.5, 128.8, 137.1, 146.5. **^{29}SiNMR** ($CDCl_3$, 600 MHz): δ (ppm) 19.47.

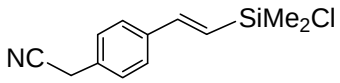
(4-methoxystyryl)chlorodimethylsilane (entry 2, Table 2).



^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.54 (s, 6H), 3.73 (s, 3H) 6.26 (d, 1H, *J*=19.2 Hz), 6.99 (d, 1H, *J*=19.2 Hz), 6.83 (d, 2H, *J*=8.4Hz), 7.36 (d, 2H, *J*=8.4Hz).**^{13}CNMR** ($CDCl_3$,

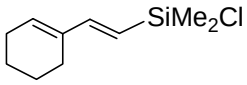
200 MHz): δ (ppm) 2.0, 55.0, 113.9, 121.5, 128.1, 129.9, 146.0, 160.2. **^{29}SiNMR** ($CDCl_3$, 600 MHz): δ (ppm) 19.52.

2-(4-((E)-2-(chlorodimethylsilyl)vinyl)phenyl)acetonitrile (entry 3, Table 2).



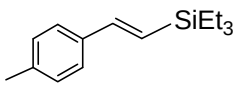
^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.56 (s, 6H), 3.67 (s, 2H) 6.45 (d, 1H, *J*=19.2 Hz), 7.05 (d, 1H, *J*=19.2Hz), 7.25 (d, 2H, *J*=8.4Hz), 7.43 (d, 2H, *J*=8.4Hz). **^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm) 1.9, 23.1, 117.5, 125.4, 127.3, 128.1, 130.4, 136.8, 145.3. **^{29}SiNMR** ($CDCl_3$, 600 MHz): δ (ppm) 19.51.

Chloro((*1E*)-2-cyclohexenylvinyl)dimethylsilane (entry 4, Table 2).



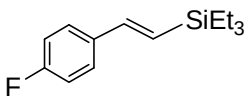
^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.49 (s, 6H), 1.62 (m, 4H) 2.14 (m, 4H), 5.66 (d, 1H, *J*=18.8Hz), 5.92 (m, 1H), 6.68 (d, 1H, *J*=18.8Hz). **^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm) 2.1, 22.3, 22.4, 23.8, 26.0, 119.7, 133.9, 136.8, 150.2.

{(*E*)-4-methylstyryl}triethylsilane (entry 5, Table 2).



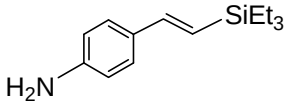
^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.94 (q, 6H, *J*=7.8Hz), 1.26 (t, 9H, *J*=7.8Hz), 2.59 (s, 3H), 6.63(d, 1H, *J*=19.2Hz), 7.14 (d, 1H, *J*=19.2Hz), 7.38 (d, 2H, *J*=8.4Hz), 7.60 (d, 2H, *J*=8.4Hz). **^{29}SiNMR** ($CDCl_3$, 600 MHz): δ (ppm) 0.38.

{(*E*)-4-fluorostyryl}triethylsilane (entry 6, Table 2).



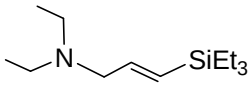
^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.83 (q, 6H, *J*=7.8Hz), 1.15 (t, 9H, *J*=7.8Hz), 6.48 (d, 1H, *J*=19.2Hz), 7.10 (d, 1H, *J*=19.2Hz), 7.25 (m, 2H), 7.55 (m, 2H). **^{29}SiNMR** ($CDCl_3$, 600 MHz): δ (ppm) 0.42.

{(*E*)-4-aminostyryl}triethylsilane (entry 7, Table 2).



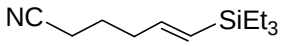
^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.50 (q, 6H, *J*=7.8Hz), 0.79 (t, 9H, *J*=7.8Hz), 3.51 (s, 2H), 6.01 (d, 1H, *J*=19.2Hz), 6.46 (d, 2H, *J*=8.4Hz), 6.64 (d, 1H, *J*=19.2Hz), 7.10 (d, 2H, *J*=8.4Hz). **^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm) 3.5, 7.3, 114.7, 120.5, 127.3, 133.2, 144.5, 146.3. **^{29}SiNMR** ($CDCl_3$, 600 MHz): δ (ppm) 0.14.

(*E*)-N,N-diethyl-3-(triethylsilyl)prop-2-en-1-amine (entry 8, Table 2).



^{1}HNMR ($CDCl_3$, 600 MHz): δ (ppm) 0.73 (q, 6H, *J*=7.8Hz), 1.08 (t, 9H, *J*=7.8Hz), 1.15 (t, 6H, J=7.2 Hz), 2.69 (q, 4H, *J*=7.2Hz), 3.33 (d, 2H, *J*=5.4Hz), 5.90 (d, 1H, *J*=18.6 Hz), 6.25 (dt, 2H, *J*=18.6Hz, *J*=5.4Hz). **^{13}CNMR** ($CDCl_3$, 200 MHz): δ (ppm) 3.4, 7.3, 11.6, 46.7, 59.3, 128.9, 145.5.

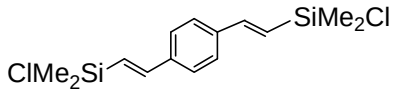
(E)-6-(triethylsilyl)hex-5-enenitrile (entry 9, Table 2)



^{1}HNMR ($CDCl_3$, 600 MHz): δ (ppm) 0.53 (q, 6H, *J*=7.8 Hz), 0.90 (t, 9H, *J*=7.8 Hz), 1.76 (quintet, 2H, *J*=5.4 Hz), 2.25 (dt, 2H, *J*=5.4 Hz, *J*=6.0 Hz), 2.30 (t, 2H, *J*=5.4 Hz), 5.63 (d, 1H, *J*=18.0 Hz), 5.92 (dt, 2H, *J*=18.0 Hz, *J*=6.0Hz). **^{13}CNMR** ($CDCl_3$, 200

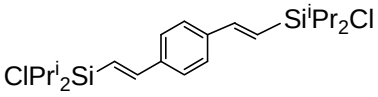
MHz): δ (ppm) 3.3, 7.2, 16.2, 24.3, 35.4, 119.5, 128.7, 145.0. **^{29}SiNMR** ($CDCl_3$, 600 MHz): -1.04.

1,4- Bis{(E)-dimethylchlorosilylethenyl}benzene (entry 1, Table 3).



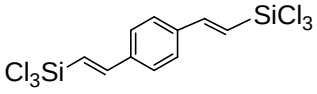
^{1}HNMR ($CDCl_3$, 200 MHz) δ 0.47(s, 12 H), 6.19 (d, 2 H, *J*=19Hz), 6.94 (d, 2H, *J*=19 Hz), 7.33 (s, 4H).

1,4- Bis{(E)-diisopropylchlorosilylethynyl}benzene (entry 2, Table 3).



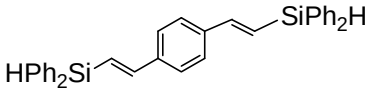
^{1}HNMR ($CDCl_3$, 200 MHz) δ 1.05 (sept, 2H, *J*=8 Hz), 1.14 (d, 24H, *J*= 3Hz), 6.39 (d, 2H, *J*=19 Hz), 7.18 (d, 2H, *J*=19 Hz), 7.48 (s, 4H). **^{13}CNMR** ($CDCl_3$, 200 MHz) δ 14.41, 17.21, 120.52, 127.54, 138.20, 148.58.

1,4- Bis{(E)-trichlorosilylethynyl}benzene (entry 3, Table 3).



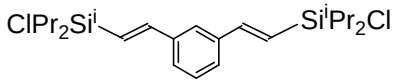
^{1}HNMR ($CDCl_3$, 200 MHz) δ 6.39 (d, 2H, *J*=18.8 Hz), 7.22 (d, 2H, *J*=18.8 Hz), 7.43 (s, 4H). **^{13}CNMR** ($CDCl_3$, 200 MHz) δ 120.5, 128.3, 137.1, 150.1. **^{29}SiNMR** ($CDCl_3$, 600 MHz): -2.1.

1,4- Bis{(E)-diphenylsilylethynyl}benzene (entry 4, Table 3).



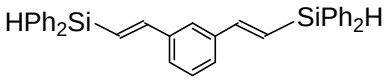
^{1}HNMR ($CDCl_3$, 200 MHz) δ 5.25 (d, 2H), 6.73 (dd, 2H), 7.11 (d, 2H), 7.36-7.61 (m, 24H).

1,3- Bis{(E)-diisopropylchlorosilylethenyl}benzene (entry 6, Table 3).



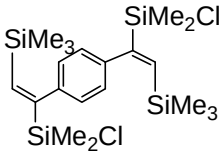
^{1}HNMR ($CDCl_3$, 200 MHz) δ 1.11 (d, 24H), 1.23 (m, 4H), 6.38 (d, 2H, *J*=19.0 Hz), 7.17 (d, 2H, *J*=19.0 Hz), 7.35-7.40 (m, 3H), 7.56 (s, 1H). **^{13}CNMR** ($CDCl_3$, 200 MHz) δ 14.08, 17.04, 120.34, 125.27, 126.92, 128.27, 137.82, 148.09 .

1,3- Bis{(E)-diphenylsilylethenyl}benzene (entry 7, Table 3).



^{1}HNMR ($CDCl_3$, 200 MHz) δ 5.25 (d, 2H), 6.62 (dd, 2H), 7.09 (d, 2H), 7.36-7.61 (m, 24H).

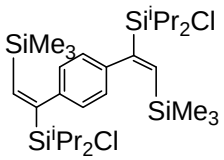
1,4- Bis{(E)-α-dimethylchlorosilyl-β-trimethylsilylethenyl}benzene (entry 1, Table 4).



^{1}HNMR ($CDCl_3$, 200 MHz) δ -0.15 (s, 18H), 0.41 (s, 12H), 6.59 (s, 2H), 6.95 (s, 4H)

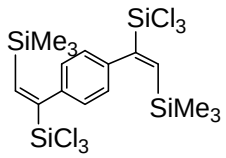
^{13}CNMR ($CDCl_3$, 200 MHzδ -0.07, 1.23, 127.32, 141.05, 148.04, 160.69. . **^{29}SiNMR** ($CDCl_3$, 600 MHz): -8.3 (-*Si*Me_3), 16.8 (*Si*Me_2Cl).

1,4- Bis{(E)-α-diisopropychlorosilyl-β-trimethylsilylethenyl}benzene (entry 2, Table 4).



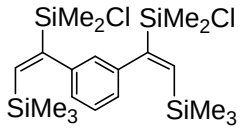
^{1}HNMR ($CDCl_3$, 200 MHz) δ -0.128 (s, 18H), 1.033 (d, 24H, J= 6.6 Hz), 1.210 (sept, 4H, J= 6.6 Hz), 6.650 (s, 2H) , 6.963 (s, 4H). **^{13}CNMR** ($CDCl_3$, 200 MHz) δ 0.20, 13.79, 17.19, 127.55, 142.05, 150.78, 157.28.

1,4- Bis{(E)-α-diisopropychlorosilyl-β-trimethylsilylethenyl}benzene (entry 3, Table 4).



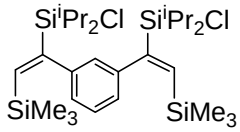
^{1}HNMR ($CDCl_3$, 200 MHz) δ - 0.192 (s, 18H), 7.04 (s, 4H), 7.18 (s, 2H). **^{13}CNMR** ($CDCl_3$, 200 MHz) δ -0.524, 129.03, 153.77, 155.36.

1,3- Bis{(E)-α-dimethylchlorosilyl-β-trimethylsilylethenyl}benzene (entry 5, Table 4).



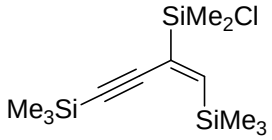
^{1}HNMR ($CDCl_3$, 200 MHz) δ -0.12 (s, 18H), 0.45 (s, 12H), 6.61 (s, 2H), 6.82-7.27 (m, 4H). **^{13}CNMR** ($CDCl_3$, 200 MHz) δ 0.01, 1.62, 126.36, 127.8, 128.3, 142.63, 148.28, 160.54.

1,3- Bis{(E)-α-diisopropylchlorosilyl-β-trimethylsilylethenyl}benzene (entry 6, Table 4).



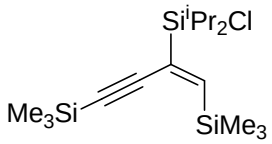
^{1}HNMR ($CDCl_3$, 200 MHz) δ -0.12 (s, 18H), 1.01 (d, 24 H), 1.23 (m, 4H), 6.58 (s, 2H), 6.87-7.34 (m, 4H).

(E)-2-(imethylchlorosilyl)-1,4-bis(trimethylsilyl)but-1-en-3-yne (entry 1, Table 5).



^{1}HNMR ($CDCl_3$, 200 MHz) δ 0.12 (s, 9H), 0.13 (s, 9H), 0.46 (s, 6H), 6.8 (s, 1H). **^{29}SiNMR** ($CDCl_3$, 600 MHz): -17.4 (-*Si*Me_2Cl), -6.9 (-*Si*Me_3), -17.8 (-*Si*Me_3).

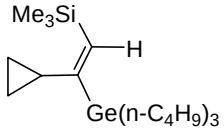
(E)-2-(imethylchlorosilyl)-1,4-bis(trimethylsilyl)but-1-en-3-yne (entry 2, Table 5).



^{1}HNMR ($CDCl_3$, 200 MHz) δ 0.062 (s, 9H), 0.161 (s, 9H), 1.038 (d, 12H, J=5.2 Hz), 1.27 (sept, 2H, J=5.7 Hz), 7.061 (s, 1H).

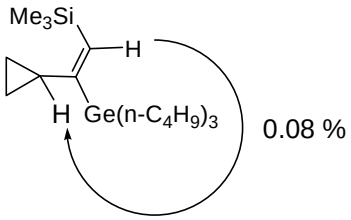
Multinuclear NMR Data of Hydrogermylated Product(s)

((*E*)-2-(Tributylgermyl)-2-cyclopropylvinyl)trimethylsilane (Scheme 7, **1**).

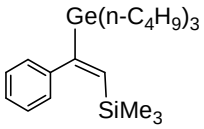


^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.13 (s, 9H), 0.46 (m, 2H), 0.65 (m, 2H), 0.83 (m, 15H), 1.28(m, 12H), 5.80 (s, 1H). **^{13}C NMR** ($CDCl_3$, 200 MHz) δ 0.4, 7.3, 13.8, 19.3, 26.6, 27.5, 28.6, 141.3, 165.0. (Yield= 99%)**.**

NOESY data.

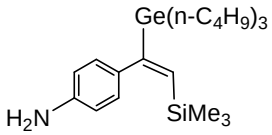


((*E*)-2-(Tributylgermyl)-2-phenylvinyl)trimethylsilane (Scheme 7, **2**)**.**



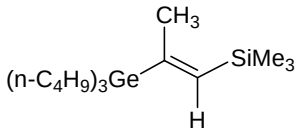
^{1}H NMR ($CDCl_3$, 200 MHz) δ -0.23 (s, 9H), 0.77 (m, 15H), 1.2 (m, 12H), 6.02 (s, 1H), 6.49-7.20 (m, 5H). **^{13}C NMR** ($CDCl_3$, 200 MHz) δ 0.5 , 12.4 , 13.8, 26.5, 27.3, 116.0 , 126.1, 126.4, 134.9, 143.5, 165.7.

4-(1-(Tributylgermyl)-2-(trimethylsilyl)vinyl)benzenamine (Scheme 7, **3**)**.**



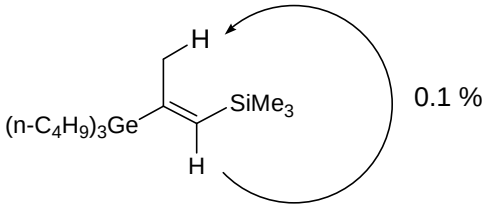
^{1}H NMR ($CDCl_3$, 200 MHz) δ -0.27 (s, 9H), 0.75 (m, 15H), 1.17 (m, 12H), 3.43 (s, 2H), 5.94 (s, 1H), 6.49 (d, 2H), 6.60 (d, 2H).

((*E*)-2-(tributylgermyl)prop-1-enyl)trimethylsilane (Scheme 7, **4**)**.**

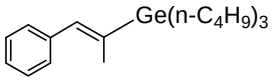


^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.01 (s, 9H), 0.77 (m, 15H), 1.20 (m, 12H), 1.81(d, 3H, *J*=1.4 Hz), 5.68 (q, 1H, *J*=1.4 Hz).

NOESY data.

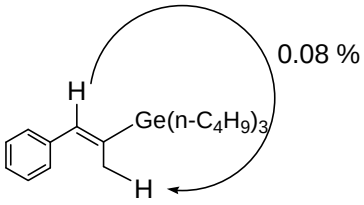


Tributyl((*E*)-1-phenylprop-1-en-2-yl)germane (Scheme 7, **5**)**.**

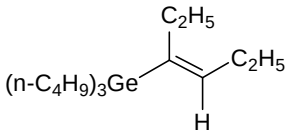


^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.88 (m, 15H), 1.31 (m, 12H), 1.98 (d, 3H,*J*= 1.6 Hz), 6.56 (d, 1H, *J*= 1.6 Hz), 6.88-7.35 (m, 5H**). ^{13}C NMR** ($CDCl_3$, 200 MHz) δ 12.4, 14.1, 18.6, 27.0, 27.8, 126.5, 127.9, 128.3, 129.2, 136.6, 138.7.

NOESY data.

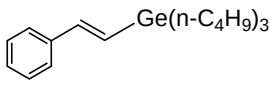


Tributyl((*E*)-hex-3-en-3-yl)germane (Scheme 5, **6**)**.**



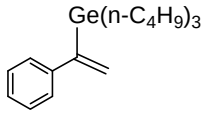
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.65 (m, 6H), 0.77 (m, 15H), 1.21 (m, 12H), 5.36 (t, 1H, *J*=6.8 Hz). **^{13}C NMR** ($CDCl_3$, 200 MHz) δ 12.6, 13.8, 14.5, 14.7, 21.3, 23.8, 26.6, 27.4, 140.0, 141.0.

Tributyl(styryl)germane (Table 10 , entry 1).



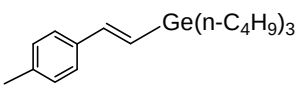
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.99 (m, 15H), 1.45 (m, 12H), 6.70 (d, 1H, *J*=19.0 Hz), 6.90 (d, 1H, *J*=19.0 Hz), 7.28-7.53 (m, 5H). **^{13}C NMR** ($CDCl_3$, 200 MHz) δ 12.95, 13.80, 26.53, 27.43, 126.15, 127.54, 128.46, 128.90, 138.49, 142.94.

Tributyl(1-phenylvinyl)germane (Table 10, entry 1).



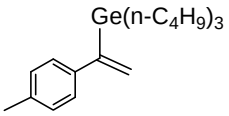
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.99 (m, 15H), 1.45 (m, 12H), 5.51 (d, 1H, *J*=2.4 Hz), 5.95 (d, 1H, *J*=2.4 Hz), 7.28-7.53 (m, 5H).

(4-Methylstyryl)tributylgermane (Table 10, entry 2).



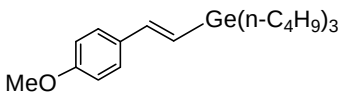
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.83 (m, 15H), 1.37 (m, 12H), 2.24 (s, 3H), 6.47 (d, 1H, *J*=19.0 Hz), 6.71 (d, 1H, *J*=19.0 Hz), 7.03(d, 2H), 7.23 (d, 2H). **^{13}C NMR** ($CDCl_3$, 200 MHz) δ 12.98, 13.80. 21.15, 26.55, 27.45, 126.07, 127.45, 129.16, 135.87, 137.30, 142.81.

Tributyl(1-p-tolylvinyl)germane (Table 10, entry 2).



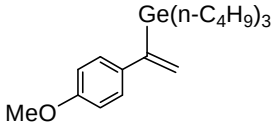
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.83 (m, 15H), 1.37 (m, 12H), 2.24 (s, 3H), 5.35 (d, 1H, *J*= 2.6 Hz), 5.78 (d, 1H, *J*= 2.6 Hz), 6.93-7.20 (m, 3H).

(4-Methoxystyryl)tributylgermane (Table 10, entry 3).



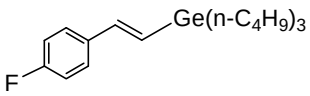
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.82 (m, 15H), 1.28 (m, 12H), 3.68 (s, 3H), 6.36 (d, 1H, *J*=19.0 Hz), 6.67 (d, 1H, *J*=19.0 Hz), 6.72-7.10 (m, 4H). **^{13}C NMR** ($CDCl_3$, 200 MHz) δ 12.96, 13. 74, 26.50, 27.42, 55.15, 113.80, 125.67, 127.27, 130.21, 131.52, 142.27.

Tributyl(1-(4-methoxyphenyl)vinyl)germane(Table 10, entry 3).



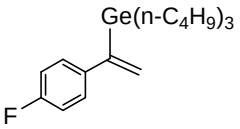
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.79 (m, 15H), 1.22 (m, 12H), 3.58 (s, 3H), 5.28 (d, 1H, *J*=2.2 Hz), 5.78 (d, 1H, *J*=19.0 Hz), 6.72-7.10 (m, 4H).

(4-Fluorostyryl)tributylgermane(Table 10, entry 4).



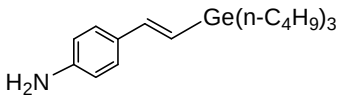
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.91 (m, 15H), 1.36 (m, 12H), 6.54 (d, 1H, *J*=18.8 Hz), 6.67 (d, 1H, *J*=18.8 Hz), 6.83(m, 2H), 7.39 (m, 2H). **^{13}C NMR** ($CDCl_3$, 200 MHz) δ 12.93, 13.78, 26.54, 27.24, 115.09, 115.51, 127.54, 128.6, 134.71, 141.62.

Tributyl(1-(4-fluorophenyl)vinyl)germane (Table 10, entry 4).



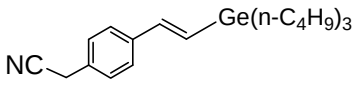
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.91 (m, 15H), 1.30 (m, 12H), 5.43 (d, 1H, *J*=2.4 Hz), 6.67 (d, 1H, *J*=2.4 Hz), 6.83-7.39 (m, 4H).

4-((E)-2-(tributylgermyl)vinyl)benzenamine (Table 10, entry 5).



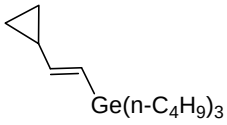
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.80 (m, 15H), 1.26 (m, 12H), 3.56 (s, 2H), 6.28 (d, 1H, *J*= 19.0 Hz), 6.52 (d, 2H, *J*= 8.0 Hz) 6.60 (d, 1H, *J*= 19.0 Hz), 7.15 (d, 2H, *J*= 8.0 Hz). **^{13}C NMR** ($CDCl_3$, 200 MHz) δ 12.9, 13.6, 26.5, 27.4, 114.9, 123.9, 127.3, 128.3, 142.6, 146.0.

2-(4-((E)-2-(tributylgermyl)vinyl)phenyl)acetonitrile (Table 10, entry 6).



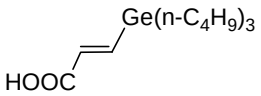
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.76 (m, 15H), 1.21 (m, 12H), 3.56 (s, 2H), 6.50 (d, 1H, *J*= 18.8 Hz), 6.66 (d, 1H, *J*= 18.8 Hz) 7.20 (m, 4H,). **^{13}C NMR** ($CDCl_3$, 200 MHz) δ 12.8, 13.7, 26.4, 23.3, 27.3, 126.8, 127.1, 127.7, 128.0, 130.3, 138.3, 141.8.

Tributyl((*E*)-2-cyclopropylvinyl)germane (Table 10, entry 7).



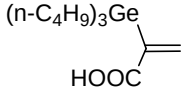
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.20 (m, 2H), 0.46 (m, 2H), 0.90 (m, 15H), 1.30 (m, 12H), 5.32 (dd, 1H), 5.75 (d, 1H). **^{13}C NMR** ($CDCl_3$, 200 MHz) δ -0.01, 7.07, 12.94, 13.76, 26.50, 27.39, 124.29, 149.37.

(*E*)-3-(Tributylgermyl)acrylic acid (Table 10, entry 8).



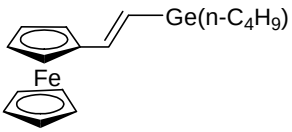
^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.77 (m, 15H), 1.21 (m, 12H), 6.13 (d, 1H, *J*=18.8 Hz), 7.52 (d, 1H, *J*=18.8 Hz), 12.10 (s, 1H). **^{13}C NMR** ($CDCl_3$, 200 MHz) δ 12.5, 13.6, 26.3, 27.2, 139.9,143.4, 170.5.

2-(Tributylgermyl)acrylic acid (Table 10, entry 8)**.**



^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.77 (m, 15H), 1.21 (m, 12H), 5.88 (d, 1H), 6.79 (d, 1H), 12.10(s, 1H). **^{13}C NMR** ($CDCl_3$, 200 MHz) δ 12.6, 13.7, 26.4, 27.2, 132.9, 154.6, 175.4.

((E)-Tributylgermyl)vinyl)ferrocene (Table 10, Entry 9).



^{1}H NMR ($CDCl_3$, 200 MHz) δ 0.78 (m, 15H), 1.25 (m, 12H), 3.95-4.34 (m, 9H), 6.04 (d, 1H, *J*=16.0 Hz), 6.38 (d, 1H, *J*=16.0 Hz). **^{13}C NMR** ($CDCl_3$, 200 MHz) δ 12.92, 13.77. 26.49, 27.46, 66.52, 68.64, 69.17, 69.20, 141.07, 124.98.

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Chapter 3

High Yield Synthesis of Silanols via Pt-nanocluster-Catalyzed Hydrolytic Oxidation of Organosilanes

3. Introduction

Silanols are compounds containing Si-OH bonds and are silicon analogues of alcohols.[1] Depending upon the numbers of hydroxy (-OH) groups attached to a particular silicon atom, organosilanols are classified in three categories such as (a) silanols, where there is only one hydroxyl group attached to a silicon atom; (b) silanediols, where there are two hydroxyl groups attached to the same silicon atom and (c) silanetriols, where there are three hydroxyl groups attached to the same silicon atom.

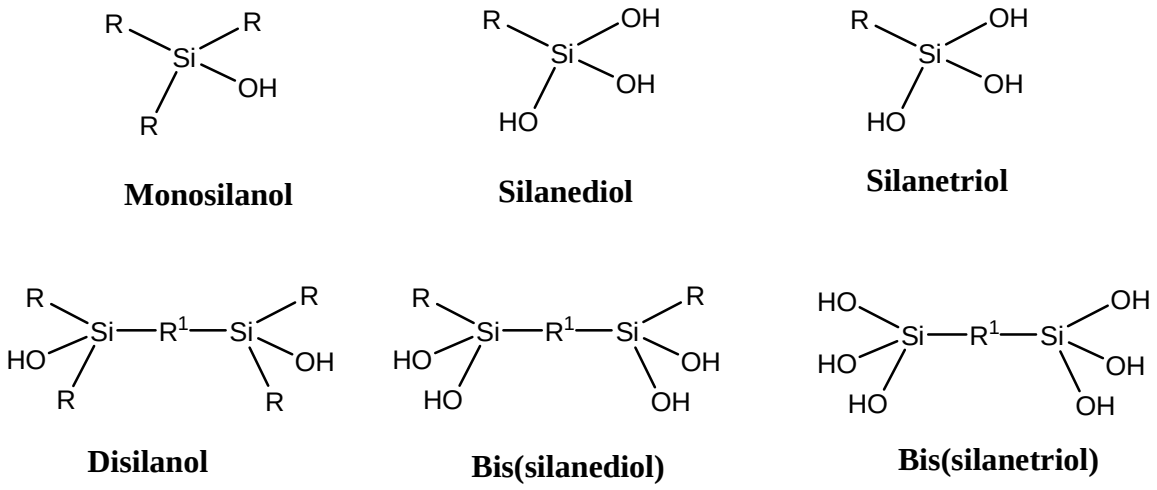


Figure 1. Various types of organosilanols.

Organosilanols find potential applications as building blocks in production of silicon-containing polymeric materials, ceramics and metallosiloxanes.[2] Besides these, organosilanols also found important applications in various organic transformations including olefin-hydroformylation,[3] cross-coupling[4] and Heck-type coupling reactions.[5] Recently, some specifically designed silanediols have been investigated and recognized as metalloprotease inhibitors. [6]

$$2R_3SiOH \longrightarrow (R_3Si)_2O + H_2O \quad \textbf{(1)}$$

Organosilanols have a general tendency to form stable siloxanes via the self-condensation reactions (eq. 1).[7] Isolation of silanols becomes very difficult when the preparative method involves the formation of such siloxane compounds. Therefore, while developing a method for the synthesis of silanols, it is highly desired to minimize the formation of such siloxane byproducts. There are a number of factors that can influence the above condensation reactions, which include, the concentration of the reaction mixture, the substrate structure and the presence of trace amount of acidic or basic impurities. Since the condensation is an intermolecular process, it has been observed that higher dilution reduces the probability of siloxane formation. The rate of condensation can also be prevented using sterically encumbered substituents on the silicon atoms, for example N-bonded silanetriol, 2,6-i-Pr_2-$C_6H_3N(SiMe_2Pr\text{-}i)Si(OH)_3$ which contains three hydroxyl group on a silicon center, is quite stable and remain unchanged for a long period.[8] The condensation of silanols to siloxanes is greatly accelerated in presence of either acid or base; it has been observed that the condensation of Si-OH can be minimized to a large extent via scavenging of the acidic or basic impurities that remain after the hydrolysis of chlorosilanes.[9]

Generally there are two general methods for the synthesis of silanols (Figure 2); (a) hydrolysis of the compounds containing Si-X group (where X = halide, carboxylate, perchlorate, sulfate, cyanate or alkoxy) and (b) oxidation of the compounds containing Si-H group.

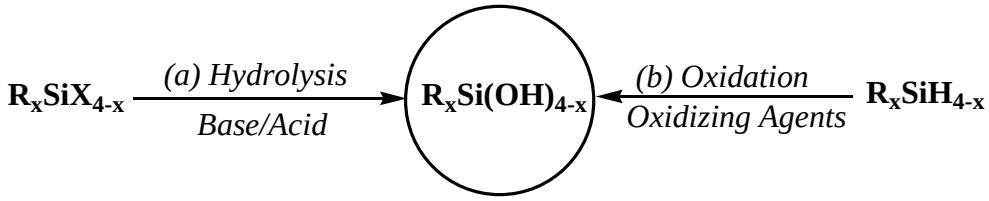


Figure 2. Two general approaches of silanols synthesis

The hydrolysis of chlorosilanes is one of the earliest methods for the synthesis of silanols.[10] Most often the hydrolysis is carried out in presence of hydrogen chloride acceptor such as aniline or triethylamine. These reactions will result in the formation of acids as by-product. Therefore, it is often very difficult to remove the trace amount of acids or base which are present in the reaction mixture and can catalyze the self-condensation of the silanol products. The organosilanes containing other functional groups such as carboxylate, perchlorate, alkoxy and triflate were known to hydrolyze to corresponding silanols. It has been found that sterically hindered silanes possessing carboxylate and perchlorate groups have greater propensity to hydrolyze to their corresponding silanols. [9]

Several oxidizing agents such as silver salt,[11] potassium permanganate,[12] perbenzoic acid,[13] ozone,[14] dioxiranes[15] and oxaziridine[16] are known to catalyze the oxidation of organosilanes containing Si-H moiety. However, these reactions are either stoichiometric or result in the formation of appreciable amounts of siloxane by-prodcuts especially when unhindered silanes are involved.[17]

Catalytic oxidation of organosilanes using various transition metal complexes such as nickel, palladium, chromium, rhodium, iridium, rhenium and copper have been extensively studied in recent years.[18] However, these protocols have limited applicability for certain organosilanes and often produce disiloxanes in significant quantity.[17]

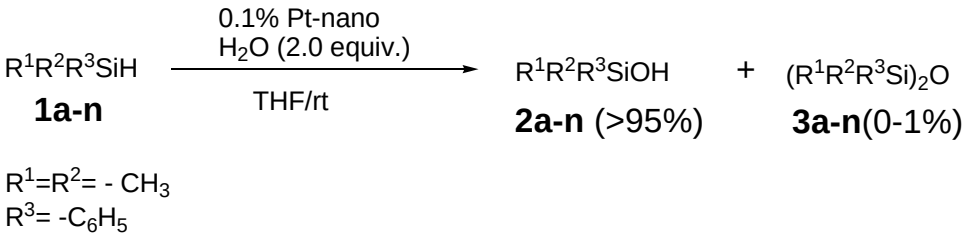
Moreover, these homogeneous catalytic systems have some drawbacks of lacking recyclability, high selectivity and product purity. Therefore, there is a strong demand to develop a heterogeneous catalytic protocol for the synthesis of silanols with high degree of selectivity and catalyst recyclability.

Recent studies from our group have revealed the potential applications of Pt-nanoclusters as an efficient and recyclable catalyst for the selective hydrosilylation and hydrogermylation of unsaturated C-C bonds (described in chapter 2). As Pt-nanoclusters do not contain either acidic or basic ligands that are responsible for the siloxane formation, we wanted to investigate the hydrolytic oxidation of organosilanes in presence of Pt-nanocluster catalysts. In this chapter, we describe hydrolytic oxidation of various organosilanes to corresponding silanols using Pt-nanocluster catalysis. In addition we also describe polymerization of bis(silanol)s to functional polysiloxanes.

3.1. Pt-nanocluster-Catalyzed Hydrolytic Oxidation of Organosilanes

In the preliminary investigation, the catalytic activity and selectivity of Pt-nanocluster catalysts in the hydrolytic oxidation of dimethylphenylsilane (**1a**) was examined (Scheme 1). The silane **1a** was chosen because its conversion to the corresponding silanol **2a** is very sensitive to the reaction conditions and often produces disiloxane **3a** as undesired side product [19]

Scheme 1. Pt-nanocluster-catalyzed selective transformation of organosilanes to silanols.



In a typical procedure, a Schlenk tube was charged with Pt-nanoclusters (0.001 mmol), THF (2 mL) and the silane **1a** (1 mmol) under positive pressure of nitrogen. To this suspension, H_2O (2.0 mmol) was added. This was accompanied by slow evolution of a gas, presumably H_2. After an interval of 5 h, complete disappearance of Si-H (δ 4.7 ppm) bond was revealed by ^{1}HNMR spectra of the crude reaction mixture. Product isolation was carried out by high-speed (30 min) centrifugation of the crude reaction mixture in hexanes (5 mL) followed by solvent evaporation. Further analysis of the isolated product by ^{13}C, ^{29}Si NMR, IR and Mass-spectroscopy has indicated exclusive formation of **2a** with no detectable amount of disiloxane **3a** (Figure 3 and 4).

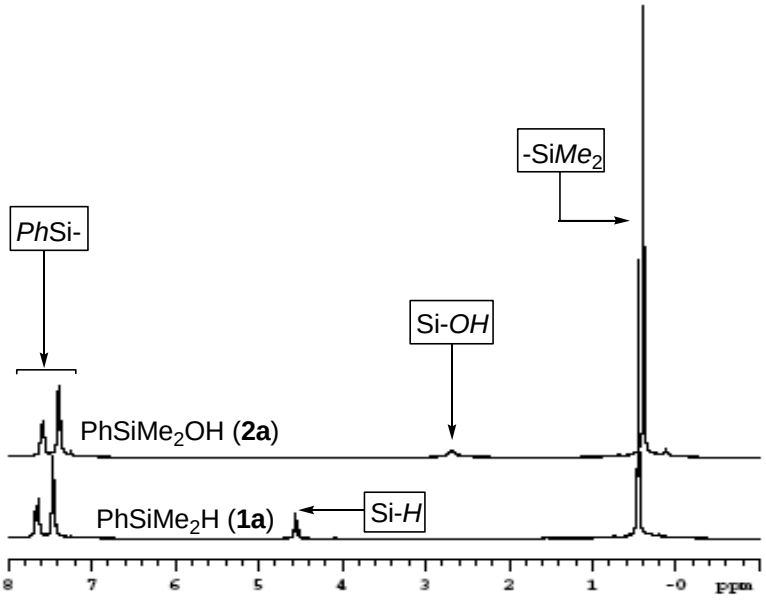


Figure 3. ^{1}H NMR of phenyldimethylsilanol **2a** (obtained from the crude reaction mixture) and phenyldimethylsilane **1a**.

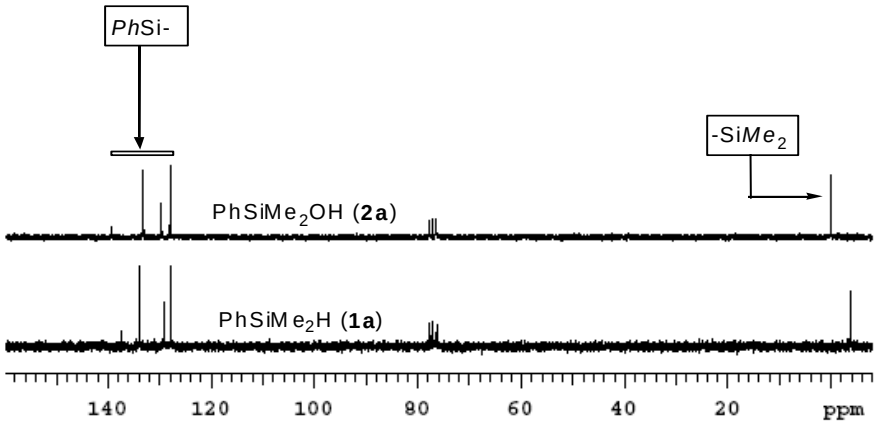


Figure 4. ^{13}C NMR of phenyldimethylsilanol **2a** (obtained from the crude reaction mixture) and phenyldimethylsilane **1a**.

To investigate the scope and limitations of the present catalysis, the oxidation of other variety of silanes has been examined using Pt-nanocluster catalysts. Under identical reaction conditions, silanes **1b-i** (Table 1) reacted with water to afford corresponding silanols **2b-i** in quantitative yield. Most of the silanes underwent oxidation reaction under room temperature except those with bulky group substituted silanes **1e** and **1f**. The reactions with these bulky silanes **1e** and **1f** required high temperature (60^0C) and longer reaction time (16-36 h) to afford the complete conversion. No formation of siloxane **3b-f** was observed irrespective of the nature of the substrates and the reaction conditions employed. Under identical conditions dihydrosilanes **1g-h** were found to afford a mixture of mono silanols and silanediols. However, an increase in water to silane ratio (8:1) provided complete conversion to corresponding silanediols **2g-h**. Phenylsilane (**1i**) containing three Si-H bonds also underwent smooth oxidation to afford phenylsilanetriol **2i**. The compounds **2a-d** were obtained as colorless liquids, while compounds **2e-i** are white solids. The compound 2i was obtained in the form of shiny white platelets and has

been stable for a year, while it is noteworthy that phenylsilanetriol synthesized using acid catalyzed hydrolysis, often resinifies with loss of water.[20] Compound **2h**, on slow evaporation from a chloroform solution, crystallized to produce colorless lathlike crystals. The single crystal X-ray analysis data matches with that of reported data of this compound.[21] The X-ray structure and crystallographic data for **2h** are given in Figure 5 and Table 2 respectively.

Table 1. Pt-nanocluster-catalyzed selective transformation of organosilanes to silanols.

Silane (entry)	Conditions[a]	Product	Yield(%)[c]
$PhMe_2SiH$ (**1a**)	5h/RT	$PhMe_2SiOH$ (**2a**)	95
$EtMe_2SiH$ (**1b**)	3h/RT	$EtMe_2SiOH$ (**2b**)	96
$t\text{-}BuMe_2SiH$ (**1c**)	4h/RT	$t\text{-}BuMe_2SiOH$ (**2c**)	95
Et_3SiH (**1d**)	8h/RT	Et_3SiOH (**2d**)	93
Ph_2MeSiH (**1e**)	16h /60^0C	$Ph_2MeSiOH$ (**2e**)	95
Ph_3SiH (**1f**)	24h /60^0C	Ph_3SiOH (**2f**)	88
Et_2SiH_2 (**1g**)	10h /RT[b]	$Et_2Si(OH)_2$ (**2g**)	96
Ph_2SiH_2 (**1h**)	36h/RT [b]	$Ph_2Si(OH)_2$ (**2h**)	92
$PhSiH_3$ (**1i**)	24h/RT	$PhSi(OH)_3$ (**2i**)	90

[a]Reagents: [Pt-nanoclusters]=0.001 mmol; [silane]= 1.0 mmol; [H_2O]= 2.0 mmol; solvent=THF (2mL) [b]Required 8.0 equiv. of H_2O.[c]Isolated Yield.

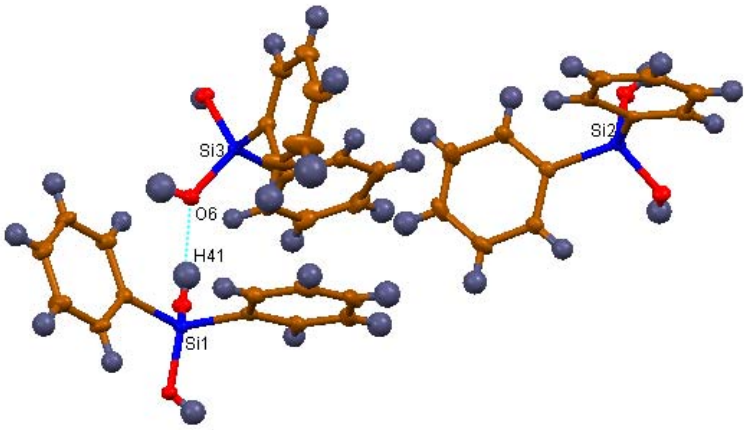


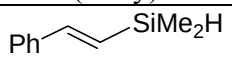
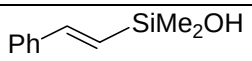
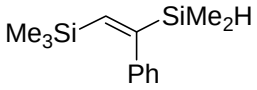
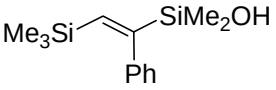
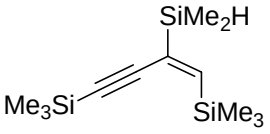
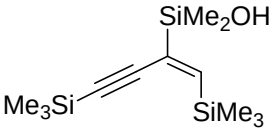
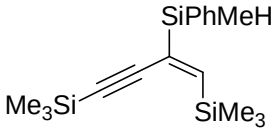
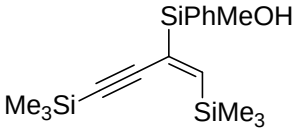
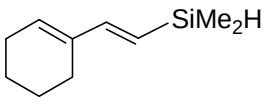
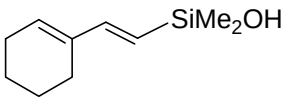
Figure 5. Single crystal X-ray structure (50 % probability displacement ellipsoids) of diphenylsilanediol (**2h**) showing hydrogen bonding between oxygen and hydrogen atom.

Table 2. Crystallographic and structure refinement data for **2h**.

Empirical Formula	$C_{12}H_{12}O_2Si$	
Crystal System	Monoclinic	
Space Group	P –1	
Unit Cell Dimensions (Ang.)	a= 9.9395 (5)	α= 110.399^o (2)
	b=14.1833 (8)	β=99.967^o (2)
	c=14.3602 (7)	γ= 108.563^o (2)
Cell Volume	1688.21	
R-factor (%)	3.42	
Temperature (K)	273	

Silanols possessing alkynyl or alkenyl group have attracted much attention because of their synthetic utilities in various organic transformations.[22] Further studies were carried out using alkene and alkyne-functionalized silanes **1j-n** (Table 3). Excellent yields (> 95%) and high selectivity (silanol: siloxane ≥ 98: 2) were achieved irrespective of the nature of the functionality present. To our surprise, though the Pt-nanoclusters are known to catalyze the hydrosilylation reaction of olefins, no hydrosilylated product was observed during the oxidation of silanes containing such olefin moieties.

Table 3. Pt-nanoclusters catalyzed hydrolytic oxidation of functional organosilanes.

Silane (entry)	Conditions[a]	Product	Yield(%)[b]
 (**1j**)	3h/RT	 (**2j**)	96
 (**1k**)	16h/RT	 (**2k**)	95
 (**1l**)	16h/RT	 (**2l**)	93
 (**1m**)	24h/RT	 (**2m**)	92
 (**1n**)	3h /60^{0}C	 (**2n**)	96

[a]Reagents: [Pt-nanoclusters]=0.001 mmol; [silane]= 1.0 mmol; [H_2O]= 2.0 mmol; solvent=THF (2mL), [c]Isolated Yield.

In recent years, arylenebis(silanol)s find potential applications as precursors to various functional polysiloxanes.[23] However, the preparation of such bis(silanol)s requires many tedious steps,[24] and it is often very difficult to achieve when variety of functional bis(silanol)s are involved. We examined hydrolytic oxidation of a series of functional bis-silanes using nanoclusters catalysis (Scheme 2). Excellent yields were obtained for all functional bis-silanes, affording selectively single bis(silanol)s **1o-s** (Table 4). Most of the products were obtained as white solids except **2r,** which was obtained as highly viscous liquid. On slow evaporation from chloroform, the compound

2o and **2p** are precipitated as needle shaped crystals. The crystal structures and crystallographic data of **2s** are presented in Figure 6 and Table 5, respectively.

Scheme 2. Hydrolytic oxidation of bis(silane)s via Pt-nanoclusters catalysis.

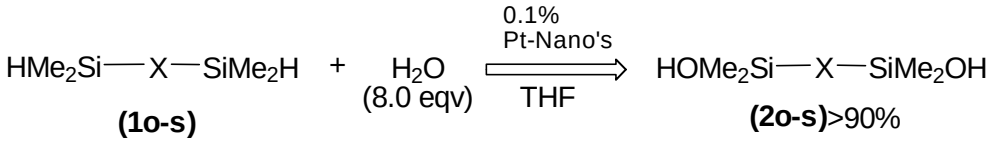
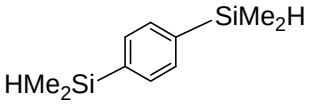
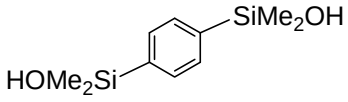
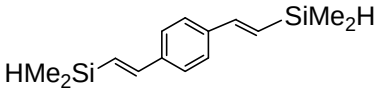
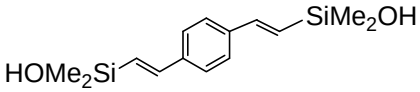
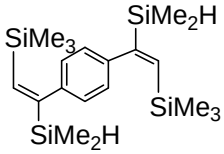
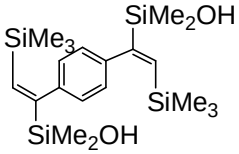
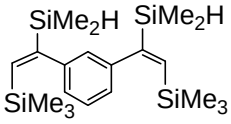
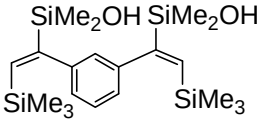
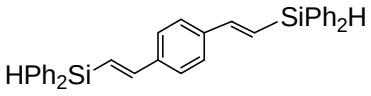
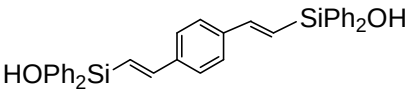


Table 4. Hydrolytic oxidation of bis(silane)s via Pt-nanocluster catalysis.

Silane (entry)	Condt.	Product	Yield (%)
 (**1o**)	6h/RT	 (**2o**)	95
 (**1p**)	6h/RT	 (**2p**)	95
 (**1q**)	24h /60 ^{0}C	 (**2q**)	92
 (**1r**)	24h /60^{0}C	 (**2r**)	95
 (**1s**)	24h /60^{0}C	 (**2s**)	92

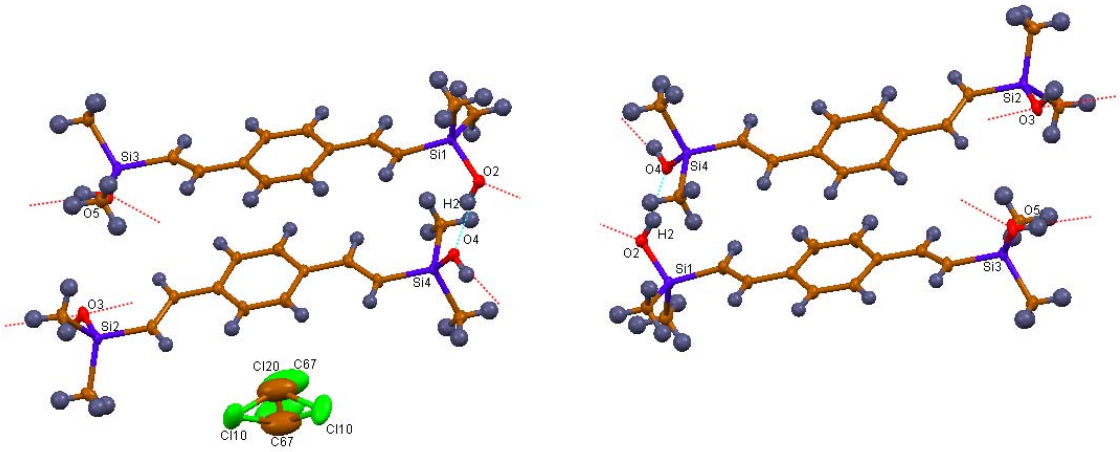


Figure 6. Single crystal X-ray structure (50 % probability displacement ellipsoids) of **2p** with a trapped $CHCl_3$ molecule.

Table 5. Crystallographic and structure refinement data for **2p**.[a]

Empirical Formula	$C_{14}H_{22}O_2Si_2$	
Crystal System	Monoclinic	
Space Group	C 2/c	
Unit Cell Dimensions (Ang.)	a= 21.8340(5)	$\alpha= 90^o$
	b= b 9.8870(3)	$\beta=105.498^o$ (1)
	c= 32.9293(9)	$\gamma= 90^o$
Cell Volume	6850.37	
R-factor (%)	3.86	
Temperature (K)	273	

[a]We are thankful to Prof. L. Roger at Rutgers University for helping with X-ray analysis.

3.2. Investigation of the Nature of True Catalysts

To gain insight in the present catalysis, investigation was carried out emphasizing TEM, UV-vis and catalyst poisoning studies. The TEM and UV-Vis studied were carried out on hydrolytic oxidation of $PhSiMe_2H$ in presence of Pt-nanoclusters (**1a**, scheme 1). Thus, after confirming ~40% progress of the reaction (confirmed by ^1H NMR), one drop of the crude reaction mixture was taken out and directly deposited on formvar/carbon-coated copper grid The TEM analysis of the sample showed presence of nanoparticle in size regime of 1-2 nm (Figure 7). The reaction was also monitored by UV-vis spectroscopy at regular intervals and showed featureless spectra, a characteristic of Pt-nanoclusters (Figure 8).

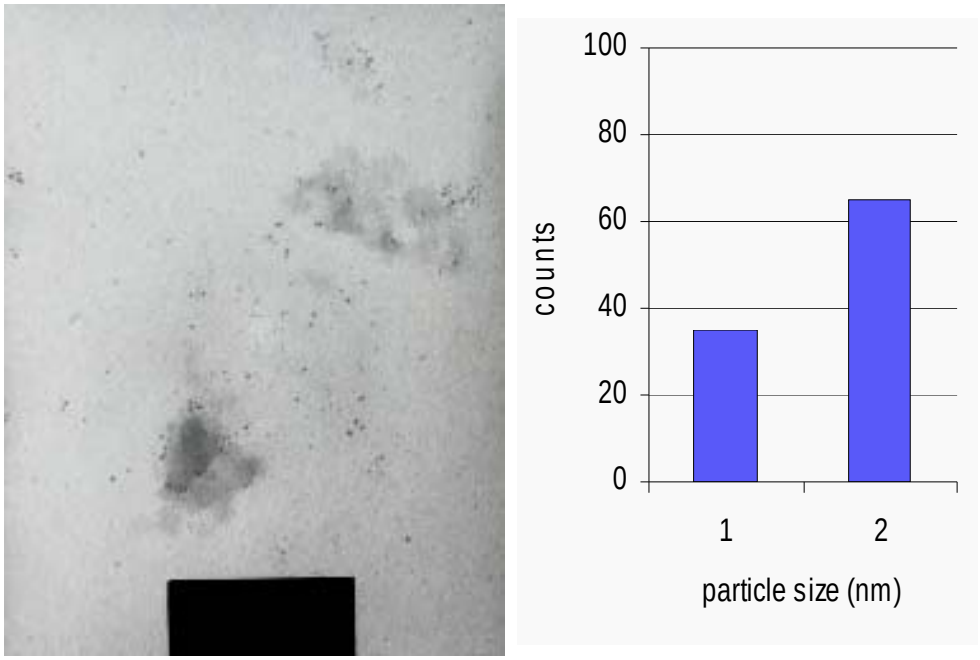


Figure 7. TEM image and particle Size analysis of the crude reaction mixture

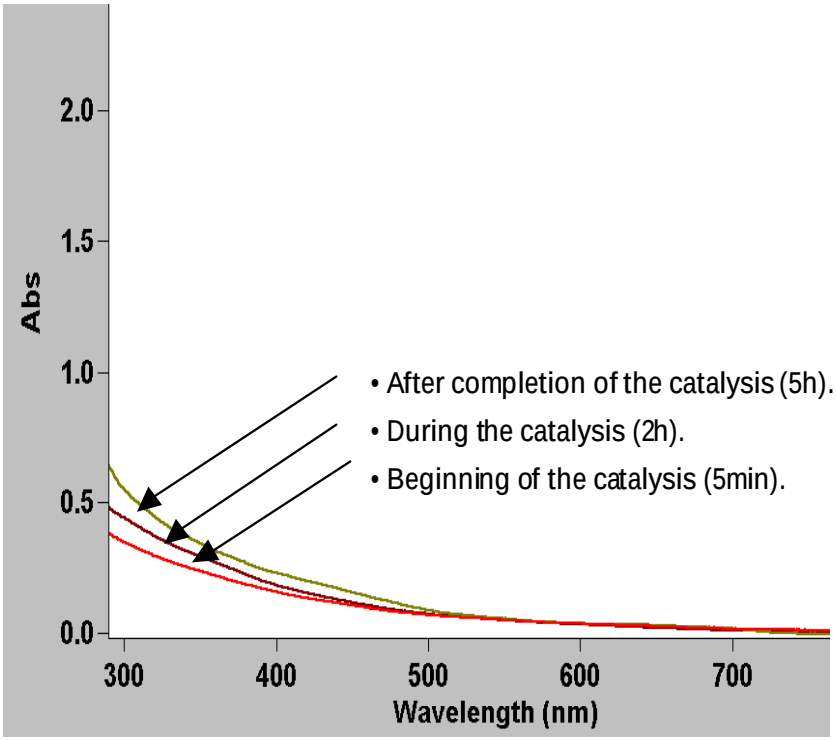


Figure 8. UV-Vis analysis of the crude reaction mixture.

Poisoning with mercury is an affirmative test for metal particle catalysis because of its ability to form alloy with the metal particles.[25] Mercury tests were typically performed by adding excess (~1.0 g) of Hg(0) to a catalytically active solution (~50% conversion). Within an hour after addition of mercury, catalysis was completely inhibited and solution turned colorless (Figure 9). No further reaction was observed even after 24h of the reaction (Figure 10).

Figure 9. The appearence of the reaction mixture before and after the addition of mercury.

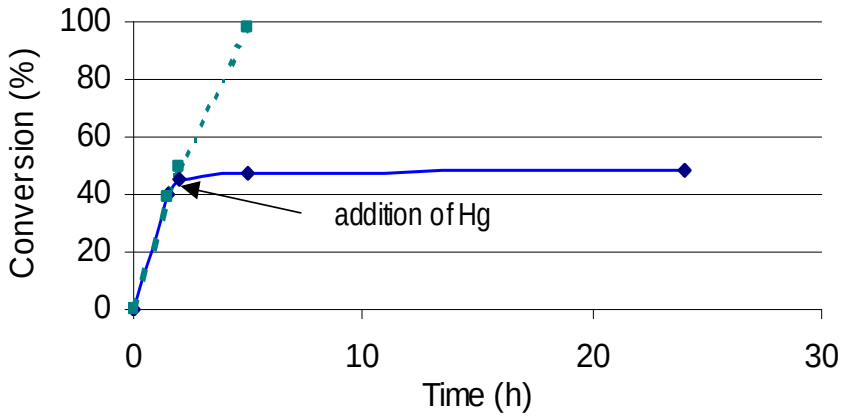


Figure 10. Poisoning of the catalysis using mercury.

The recyclability of Pt-nanocluster catalyst is one of the important advantageous properties over the homogeneous catalysis. The recyclability of the present catalyst was tested in the following way: after removing the solvent, the crude reaction mixture (**1a**, Scheme 1) was redissolved in hexanes (5 mL) and centrifuged for 30min. while the catalyst was precipitated quantitatively. The isolated catalyst, after drying under high vacuum was again recharged with silane **1a** (1 mmol) and water (2 mmol) in THF (2 mL) and the reaction mixture was stirred at room temperature to achieve complete conversion

(5 h). Additional three cycles were achieved reusing the same batch of catalyst without significant loss of activity and selectivity.

Since a number of platinum metal complexes are known to catalyze Si-H transformation reactions, we investigated the catalytic activity of most common platinum complexes and compared the result with those for the present nanocluster catalytic system. Thus, under the standard reaction conditions (Scheme 1), the silane **1a** was hydrolytically oxidized using a series of Pt-metal complexes. A comparative study of activity and selectivity of various platinum complexes is presented in Table 6 (entry 3-8). All the catalysts were found to be more or less active, but led to the mixtures of corresponding silanols and disiloxanes.

Table 6. Hydrolytic oxidation of dimethylphenylsilane using various platinum metal catalysts.

Ent	Catalyst (0.1 mol %)	Reaction Conditions	Conversion (%) [a]	Silanol/ Disiloxane[b]
1	None	12h/THF/RT	no reaction	n.a.
2	Pt-nano's	5h/THF/RT	99	>99: 01
3	PtO_2	12h/THF/RT	90	60: 40
4	H_2PtCl_6	12h/THF/RT	80	75: 25
5	$(COD)PtCl_2$	12h/THF/RT	98	50: 50
6	(COD)Pt Me_2	12h/THF/RT	99	75: 25
7	Pt(dvs)	12h/THF/RT	85	95: 05
8	Pt/C	12h/THF/RT	88	90: 10

[b]Conversion was determined by ^1H NMR. [c]Product ratio's were determined by the ^1H NMR of the crude reaction mixtures, (dvs: $H_2C{=}CHSiMe_2OSiMe_2CH{=}CH_2$).

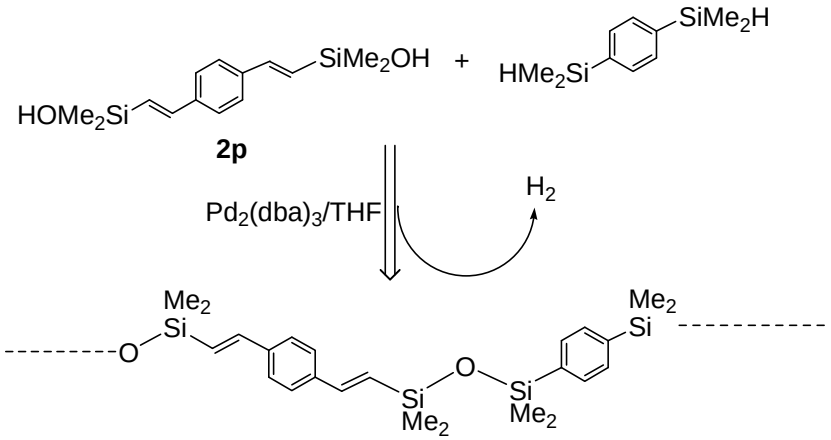
3.3. Dehydrocoupling Polymerization of Bis(silanol)s

Dehydrocoupling polymerization of bis-silanes with hydrogen containing compounds is one of the most efficient methods for synthesizing polysiloxanes. A number of transition metal catalysts including $Pd_2(dba)_3$ (where dba=dibenzyledeneacetone), $PdCl_2$, Pd/C, H_2PtCl_6, $Pt(PPh_3)_4$, $[RhCl(COD)]_2$ and $RhCl(PPh_3)_3$ are known to catalyze these polymerization reactions. Among these $Pd_2(dba)_3$ has been reported as most effective catalyst for dehydrocoupling reactions.[23c-d] Recently, $B(C_6F_5)_3$ has also been used as catalyst to synthesize optically active polysiloxanes via dehydrocoupling reactions of optically active bis(silanol)s with bis-silanes.[26] Although, there have been few reports on catalytic dehydrocoupling reactions, the synthesis of polysiloxanes using various bis(silanol)s is still impeded due to the limited availability of bis(silanol)s. Since Pt-nanocluster-catalyzed hydrolytic oxidation of organosilanes has given access to variety of functional bis(silanol)s, we were prompted to study the dehydrocoupling of such functional bis(silanol)s.

In a preliminary investigation, the dehydrocoupling of **2p** with bis(dimethylsilyl)benzene (**1o)** was examined using $Pd_2(dba)_3$ as a catalyst (Scheme 3). A 25 mL round-bottom flask was charged with $Pd_2(dba)_3$ (0. 005 mmol) and **2p** (1.0 mmol) under nitrogen atmosphere. To this mixture, distilled toluene (4.0 mL) and bis(dimethylsilyl)benzene (1.0 mmol) were consecutively added and the reaction mixture was allowed to stir at 40 ^{0}C. The addition of bis-silane was accompanied by immediate evolution of a gas, presumably hydrogen gas. After 10 h, the reaction was stopped and the entire reaction mixture was poured into cold methanol (10 mL), affording the product as colorless viscous liquid. The product was dried under vacuum and analyzed by NMR

and GPC. The GPC and NMR result revealed the formation of polymer with a molecular weight of 10,000 g/mol. However, appearance of two new peaks at 0.9 ppm and 2.5 ppm in the ^{1}H NMR clearly indicated the hydrogenation of C-C double bond occurred in the silanol moiety (Figure 11).

Scheme 3. Catalytic dehydrocoupling polymerization of **2p** with bis(dimethylsilyl)benzene.



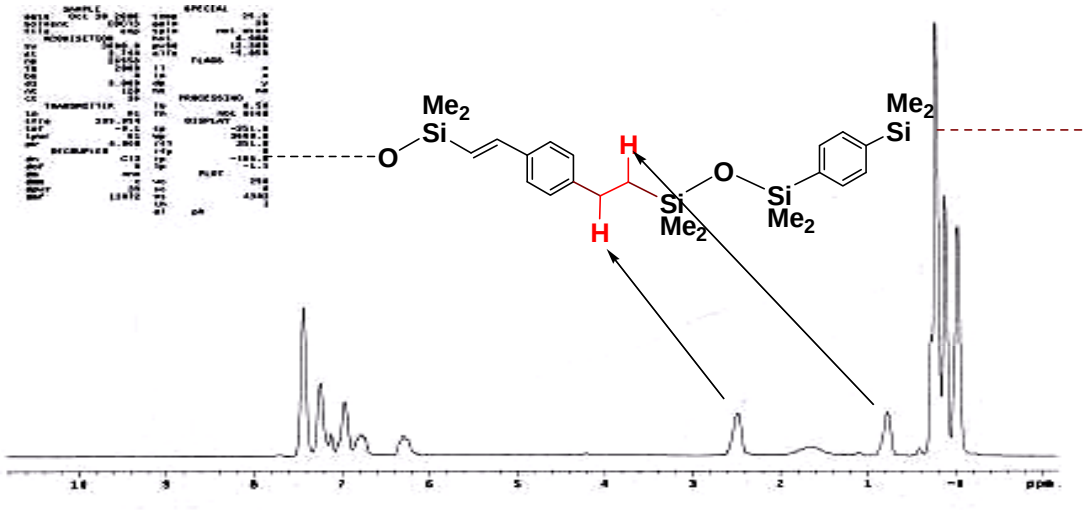


Figure 11. ^{1}H NMR spectra of the polymer obtained using $Pd_2(dba)_3$ catalyst.

The same reaction was also studied using other existing catalysts such as $RhCl(PPh_3)_3$, $B(C_6F_5)_3$ and Pt-nanoclusters. The results are summarized in Table 7. Among the catalytic systems studied, $B(C_6F_5)_3$ appeared to be the most efficient catalyst, affording the polymer with highest selectivity (no hydrogenation was observed in ^1H NMR, Figure 12).

Table 7. Dehydrocoupling polymerization of **2p** in presence of various catalysts (Catalyst comparison).

Catalysts	Conc. (mol%)	Condition	Yield (%)	Mol. Wt. (Dalton)	PDI	Hydrogenation (%)
$Pd_2(dba)_3$	0.5	40 ^{0}C/24h	80	10000	2.5	60
$RhCl(PPh_3)_3$	0.5	40 ^{0}C/24h	No reaction	----	----	X
$B(C_6F_5)_3$	0.5	40 ^{0}C/24h	90	12600	1.5	X
Pt-nano	0.5	40 ^{0}C/24h	No reaction	----	----	X

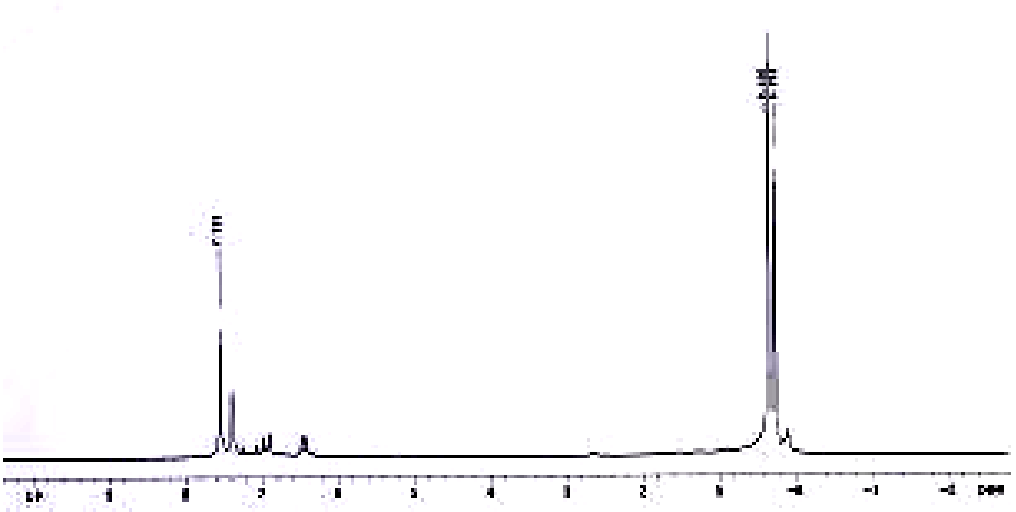
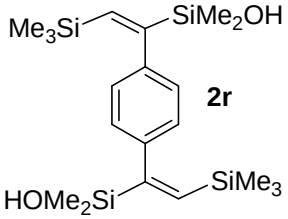
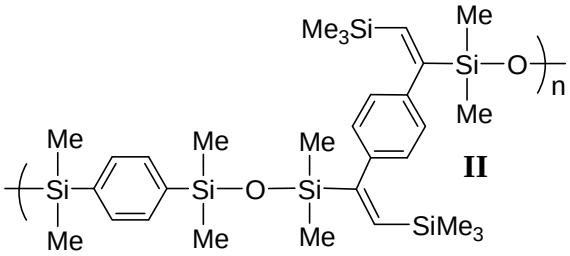
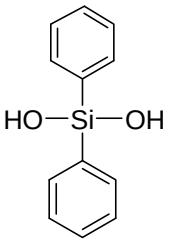
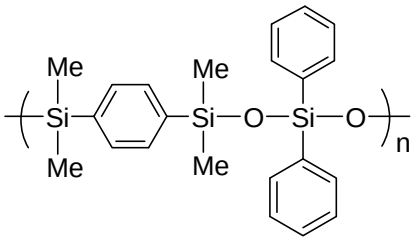
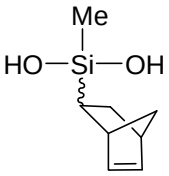
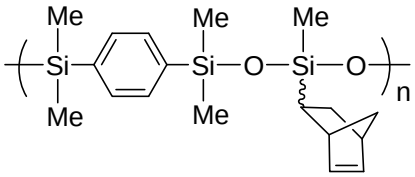
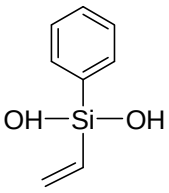
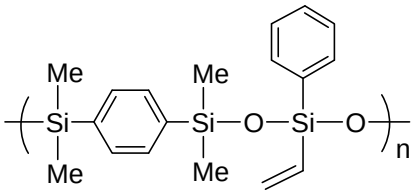


Figure 12. ^1H NMR spectra of the polymer **I** obtained using $B(C_6F_5)_3$ catalyst.

Further studies were carried out using other functional bis(silanol)s with $B(C_6F_5)_3$ as catalyst. A series of functional bis(silanol)s underwent polymerization without significant hydrogenation of olefin bonds. The molecular of weights of the synthesized polymers were in the range of 5000-10000 g/mol with polydispersity in the range of 1.3-1.7. In case of polymer **III**, the lower molecular weight and high polydisperisty can be attributed to the lower reactivity of diphenylsilanols.[23d]

Table 8. Dehydrocoupling polymerization of functional bis(silanol)s with bis(dimethylsilyl)benzene using $B(C_6F_5)_3$ catalyst.

Bis(silanol)s	Polymer structure	Yield	Mol. Wt.	PDI
 **2r**	 **II**	80	9500	1.4
 **2h**	 **III**	40	2100	3.3
 **2u**	 **IV**	70	5300	1.7
 **2v**	 **V**	85	7000	1.6

3.4. Conclusion

In this chapter, Pt-nanocluster-catalyzed, highly efficient, mild and selective transformation of organosilane to corresponding silanols is described. Various olefin-functionalized mono and bis(silanol)s are produced in excellent yield under a mild reaction condition. In situ investigations using different spectroscopic techniques have revealed participation of Pt-nanocluster in the selective transformation. A comparative study of catalytic activities of various Pt-metal complexes has shown that Pt-nanocluster is one of the most efficient catalysts affording silanol with excellent selectivity and high yields. The polymerization of the functional bis(silanol)s was studied using various transition-metal and $B(C_6F_5)_3$ catalysts. $B(C_6F_5)_3$ was found to be the most effective and selective catalyst for polymerization without disturbing the functional groups present in the silanols.

3.5. Experimental Section

General Aspects. All of the experiments and manipulations were performed under a positive pressure of dry argon or nitrogen using standard Schlenk-tube techniques. Solvent were purchased from EM science (Merck) and distilled over sodium/benzophenone before use. PMHS (Mw ≈ 2000), $Me_2Pt(COD)$ and silanes **1a-h** were purchased from Aldrich Chemical Co. and Gelest Chemical Co. and used as received. The functional silanes **1j-n and 1p-s** were synthesized via Pt-nanocluster-catalyzed hydrosilylation[1] of functional alkynes with dimethylchlorosilane followed by reduction of the chloro products using $LiAlH_4$. Compound **2u** and **2v** were synthesized via hydrolysis of corresponding chlorosilane. All alkynes were purchased from GFS Chemical Co. and used as received. ^1H NMR, ^{13}C NMR and ^{29}Si NMR spectra were

recorded on 200 MHz and 600 MHz Varian Unity NMR instruments. Spectra were referenced internally to the corresponding solvent shifts. Philips CM 100 transmission electron microscope (TEM) was employed to examine the reaction mixture for the presence of Pt-nanoclusters. Scanning electron microscope Amray 1910 (SEM) was used to analyze solid Pt-nanoclusters.

General Procedure For Hydrolytic Oxidation of Organosilanes. A Schlenk tube was charged with Pt-nanoclusters (0.005 g, 0.001 mmol Pt) and flushed thoroughly with dry nitrogen. To this solid catalyst, dry THF (2 mL), silane (1.0 mmol) and H_2O (2.0 mmol) were added consecutively and the reaction mixture was stirred at room temperature (5-15 h). The brown viscous liquid obtained after solvent evaporation was re-dissolved in hexane and centrifuged to obtain a clear solution. Removal of hexane from this clear solution led to analytically pure product (90-98%).

General Procedure For Hydrolytic Oxidation of Bis-silanes. A schlenk tube was charged with Pt-nanoclusters (0.005 g, 0.001 mmol Pt) and flushed thoroughly with dry nitrogen. To this solid catalyst, dry THF (2 mL), silane (1.0 mmol) and H_2O (8.0 mmol) were added consecutively and the reaction mixture was stirred at room temperature (5-15 h). The brown viscous liquid/solid obtained after solvent evaporation was re-dissolved in hexane/benzene and centrifuged to obtain a clear solution. Removal of hexane from this clear solution led to analytically pure product (90-98%).

Mercury Poisoning Studies. Two Schlenk tubes were charged with Pt-nanoclusters (0.005 g, 0.001 mmol) and flushed thoroughly with dry nitrogen. To this solid catalyst, dry THF (2 mL), $PhMe_2SiH$ (1.0 mmol) and H_2O (2.0 mmol) were added consecutively and the reaction mixture was stirred at room temperature. After an interval of 2 h, an

aliquot (0.2 mL) of the crude reaction mixtures were taken out and analyzed by NMR, which indicated ~50% conversion of silane to silanol. An excess Hg (1.0 g) was added to one of the reaction mixtures, the solution turned colorless after the addition of mercury The reactions were monitored using NMR upto 24 h. In absence of mercury, the reaction was completed in 5 h, but no significance progress was observed with Hg poisoned reaction upto 24 h.

3.5.1. Preparation and characterization of functional silanes (1j-1n and 1p-1s)

(*E*)-Dimethyl(2-phenylethenyl)silane (1j, Table 3**).** A Schlenk tube was charged with Pt-nanoclusters (0.010 g, 0.002 mmol) and flushed with nitrogen. Dry benzene (5 mL) and phenylacetylene (0.436 mL, 4.0 mmol) were added consecutively. To this suspension, dimethylchlorosilane (0.66 mL, 6.0 mmol) was added and the mixture was allowed to stir continuously. After 6 h, the reaction mixture was monitored by NMR, which indicated quantitative conversion of alkyne to corresponding hydrosilylated product. After removing the solvent (benzene) using high vacuum technique, diethyl ether (60 mL) and $LiAlH_4$ (0.228 g, 6.0 mmol) were slowly added at 0^0C. The resulting reaction mixture was allowed to warm up to room temperature over 6 h with stirring. The reaction mixture was poured in ice (30 gm) and the product was extracted with diethyl ether (20 mL x 2), washed with brine (20 mL) and dried over Na_2SO_4. Solvent evaporation of this mixture afforded **1j** (*E*)-Dimethyl(2-phenylethenyl)silane (0.58 g, 90%) as yellow viscous liquid. ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.13 (d, 6H, *J*= 3.8 Hz), 4.08 (m, 1H), 6.34 (dd, 1H, *J*=19.0 Hz, 2.6 Hz), 6.85 (d, 1H, *J*=19.0 Hz), 6.81-7.34 (m, 5H). ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm)-4.0, 126.03, 126.2, 128.1, 128.5, 138.1, 145.3. ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm)-19.8 (d, J_{Si-H}= 186.5 Hz).

((*E*)-Dimethyl[2-(trimethylsilyl)phenylethenyl)silane (1k, Table 3**).** A schlenk tube was charged with Pt-nanoclusters (0.005 g, 0.001 mmol) and flushed with nitrogen. Dry benzene (5 mL) and trimethylsilylethynylbenzene (0.392 mL, 2.0 mmol) were added consecutively. To this suspension, dimethylchlorosilane (0.44 mL, 4.0 mmol) was added and the mixture was allowed to stir continuously. After 24 h, the reaction mixture was monitored by NMR, which indicated formation of hydrosilylated product in quantitative yield. To this crude product obtained, diethyl ether (60 mL) and $LiAlH_4$ (0.114 g, 3.0 mmol) were slowly added at 0^0C. The resulting reaction mixture was allowed to warm up to room temperature over 6 h with stirring. The reaction mixture was poured in ice (30 gm) and the product was extracted with diethyl ether (20mL x 2), washed with brine (20 mL) and dried over Na_2SO_4. Solvent evaporation of this mixture afforded **1k** ((*E*)-dimethyl[2-(trimethylsilyl)phenylethenyl)silane (0.41 g, 88%) as colorless liquid. ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) -0.13 (s, 9H), 0.16 (d, 6H, *J*= 3.6 Hz)), 4.21 (sept, 1H, *J*= 3.6Hz), 6.46 (s, 1H), 7.04-7.39 (m, 5H). ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm)-4.2, 0.10, 126.0, 127.3, 127.9, 145.0, 146.1, 163.6. ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) -9.4, -14.9 (d, J_{Si-H}= 193.5 Hz).

Compound 1l (Table 3)**.** To a schlenk tube charged with Pt-nanoclusters (0.020 g, 0.004 mmol) bis(trimethylsilyl)butadiyne (1.94 g, 10.0 mmol) and benzene (20 mL) were added consecutively. To this suspension, dimethylchlorosilane (1.65 mL, 15.0 mmol) was added and the mixture was allowed to stir continuously. After 24 h, the reaction mixture was monitored by NMR, which indicated formation of mono-hydrosilylated product in quantitative yield. To this crude product obtained, diethyl ether (80 mL) and $LiAlH_4$ (0.57 g, 15.0 mmol) were slowly added at 0^0C. The resulting reaction mixture was

allowed to warm up to room temperature over 6 h with stirring. The reaction mixture was poured in ice (60 g) and the product was extracted with diethyl ether (50 mL x 2), washed with brine (50 mL) and dried over Na_2SO_4. Solvent evaporation of this mixture afforded **1l** (2.31g, 91%) as yellowish liquid. ^{1}HNMR ($CDCl_3$, 600 MHz): δ (ppm) 0.16 (s, 18H), 0.19 (d, 6H, *J*=3.0 Hz), 4.0 (sept, 1H, *J*=3.0 Hz), 6.65 (s, 1H). ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm)-4.6, -1.0, -0.1, 96.0, 107.0, 139.6, 157.7. ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) -8.1(-*Si*Me_3), -13.6 (d,-*Si*Me_2H, J_{Si-H}= 194.2 Hz), -18.3 (-*Si*Me_3).

Compound 2m (Table 3). To a Schlenk tube charged with Pt-nanoclusters (0.020 g, 0.004 mmol) bis(trimethylsilyl)butadiyne (1.94 g, 10.0 mmol) and benzene (20 mL) were added consecutively. To this suspension, phenylmethylchlorosilane (1.48 mL, 10.0 mmol) was added and the mixture was allowed to stir continuously. After 24 h, the reaction mixture was monitored by NMR, which indicated formation of mono-hydrosilylated product in quantitative yield. To this crude product obtained, diethyl ether (80 mL) and $LiAlH_4$ (0.57 g, 15.0 mmol) were slowly added at 0^0C. The resulting reaction mixture was allowed to warm up to room temperature over 6 h with stirring. The reaction mixture was poured in ice (60 g) and the product was extracted with diethyl ether (50 mL x 2), washed with brine (50 mL) and dried over Na_2SO_4. Solvent evaporation of this mixture afforded **1m** (2.84g, 90%) as yellowish liquid. ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.09 (s, 9H), 0.11 (s, 9H), 0.43 (d, 6H, *J*=3.8 Hz), 4.52 (sept, 1H, *J*=3.8 Hz), 6.66 (s, 1H), 7.28 (m, 3H), 7.53 (m, 2H). ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm)-5.6, -1.1, -0.2, 95.1, 106.5, 127.8, 129.6, 134.5, 134.8, 139.9, 159.7. ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) -8.8(-*Si*Me_3), -16.0 (d,-*Si*Me_2H, J_{Si-H}= 204.5 Hz), -19.3 (-*Si*Me_3).

((1*E*)-2-cyclohexenylvinyl)dimethylsilane (1n, Table 3**).** A Schlenk tube was charged with Pt-nanoclusters (0.010 g, 0.002 mmol) and flushed with nitrogen. Dry benzene (5 mL) and 1-ethynylhexene (0.470 mL, 4.0 mmol) were added consecutively. To this suspension, dimethylchlorosilane (0.66 mL, 6.0 mmol) was added and the mixture was allowed to stir continuously. After 6 h, the reaction mixture was monitored by NMR, which indicated complete hydrosilylation of triple bond. To this crude product obtained, diethyl ether (60 mL) and $LiAlH_4$ (0.114 g, 3.0 mmol) were slowly added at 0^0C. The resulting reaction mixture was allowed to warm up to room temperature over 6 h with stirring. The reaction mixture was poured in ice (30 g) and the product was extracted with diethyl ether (20mL x 2), washed with brine (20 mL) and dried over Na_2SO_4. Solvent evaporation of this mixture afforded **1n** ((1*E*)-2-cyclohexenylvinyl)dimethylsilane (0.62g, 93%) as light yellow liquid. ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.01 (d, 6H, *J*= 3.6Hz), 1.49 (m, 4H), 2.0 (m, 4H), 3.97 (sept, 1H, *J*= 3.6Hz), 5.52 (dd, 1H, *J*= 18.0 Hz, 3.6Hz), 5.68 (m, 1H), 6.45 (d, 1H, *J*= 18.0 Hz). ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm)- 3.9, 22.4, 22.6, 23.9, 25.9, 120.8, 128.3, 131.5, 137.2, 149.1. ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) -20.3 (d, J_{Si-H}= 187.1 Hz).

Compound 1p (Table 4**).** A schlenk tube was charged with Pt-nanoclusters (0.010 g, 0.002 mmol) and 1,4-diethynylbenzene (0.252 g, 2.0 mmol) under the flow of nitrogen. To this mixture, dry benzene (5 mL) and dimethylchlorosilane (0.66 mL, 6.0 mmol) was added consecutively and the mixture was allowed to stir continuously. After 24 h, the reaction mixture was monitored by NMR, which indicated quantitative conversion of alkyne to corresponding hydrosilylated product. After removing the solvent (benzene) using high vacuum technique, diethyl ether (60 mL) and $LiAlH_4$ (0.228 g, 6.0 mmol)

were slowly added at 0^0C. The resulting reaction mixture was allowed to warm up to room temperature over 6 h with stirring. The reaction mixture was poured in ice (30 g) and the product was extracted with diethyl ether (20 mL x 2), washed with brine (20 mL) and dried over Na_2SO_4. Solvent evaporation of this mixture afforded **1p** (0.47 g, 95%) as yellow viscous liquid. ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.12 (d, 12H, *J*= 3.8 Hz), 4.13 (m, 2H), 6.32 (dd, 2H, *J*=19.0 Hz, 2.6 Hz), 6.76 (d, 2H, *J*=19.0 Hz), 7.24 (s, 4H).. ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm)-20.9 (d, J_{Si-H}= 186.5 Hz).

Compound 1q (Table 4**).** A schlenk tube was charged with Pt-nanoclusters (0.010 g, 0.002 mmol) and 1,4-bis(trimethylsilylethynyl)benzene (0.540 g, 2.0 mmol) under the flow of nitrogen. To this mixture, dry benzene (5 mL) and dimethylchlorosilane (0.66 mL, 6.0 mmol) was added consecutively and the mixture was allowed to stir continuously. After 48 h, the reaction mixture was monitored by NMR, which indicated quantitative conversion of alkyne to corresponding hydrosilylated product. After removing the solvent (benzene) using high vacuum technique, diethyl ether (60 mL) and $LiAlH_4$ (0.228 g, 6.0 mmol) were slowly added at 0^0C. The resulting reaction mixture was allowed to warm up to room temperature over 6 h with stirring. The reaction mixture was poured in ice (30 g) and the product was extracted with diethyl ether (20mL x 2), washed with brine (20 mL) and dried over Na_2SO_4. Solvent evaporation of this mixture afforded **1q** (0.72 g, 93%) as colorless viscous liquid. ^{1}HNMR ($CDCl_3$, 200 MHz): ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) -0.19 (s, 18H), 0.02 (d, 12H, *J*= 3.6 Hz)), 4.10 (sept, 2H, *J*= 3.6Hz), 6.33 (s, 2H), 6.83 (s, 4H). ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm)-4.6, -0.1, 126.4, 142.2, 145.5, 163.2. ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) -9.5 (s), -15.2 (d, J_{Si-H}= 188.6 Hz).

Compound 1r (Table 4**).** A Schlenk tube was charged with Pt-nanoclusters (0.010 g, 0.002 mmol) and 1,3-bis(trimethylsilylethynyl)benzene (0.540 g, 2.0 mmol) under the flow of nitrogen. To this mixture, dry benzene (5 mL) and dimethylchlorosilane (0.66 mL, 6.0 mmol) was added consecutively and the mixture was allowed to stir continuously. After 48 h, the reaction mixture was monitored by NMR, which indicated quantitative conversion of alkyne to corresponding hydrosilylated product. After removing the solvent (benzene) using high vacuum technique, diethyl ether (60 mL) and $LiAlH_4$ (0.228 g, 6.0 mmol) were slowly added at 0^0C. The resulting reaction mixture was allowed to warm up to room temperature over 6 h with stirring. The reaction mixture was poured in ice (30 g) and the product was extracted with diethyl ether (20 mL x 2), washed with brine (20 mL) and dried over Na_2SO_4. Solvent evaporation of this mixture afforded **1r** (0.75 g, 97%) as colorless viscous liquid. ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) -0.13 (s, 18H), 0.2 (d, 12H, *J*= 3.6 Hz)), 4.09 (sept, 2H, *J*= 3.6Hz), 6.30 (s, 2H), 6.61(s, 1H), 6.50 (d, 2H, *J*=7.6 Hz), 7.08 (t, 1H, *J*=7.6 Hz). ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm)-4.1, 0.2, 125.2, 125.5, 127.4, 144.6, 145.8, 163.4. ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) -10.8(s), -12.9 (d)

Compound 1s (Table 4**).** A Schlenk tube was charged with Pt-nanoclusters (0.010 g, 0.002 mmol) and 1,4-diethynylbenzene (0.252 g, 2.0 mmol) under the flow of nitrogen. To this mixture, dry benzene (5 mL) and diphenylsilane (0.37g, 4.0 mmol) was added consecutively and the mixture was allowed to stir continuously. After 48 h, the reaction mixture was monitored by NMR, which indicated quantitative conversion of alkyne to corresponding hydrosilylated product. After removing the solvent (benzene) using high vacuum technique, the product **1s** was obtained as highly viscous liquid (0.91g, 93%).

^{1}HNMR ($CDCl_3$, 200 MHz): ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 5.06 (d, 2H, *J*=2.4 Hz), 6.52 (dd, 2H, *J*= 19.0 Hz, *J*= 2.4 Hz)), 7.0 (d, 2H, *J*= 19.0 Hz), 7.2-7.56 (m, 19H).

Compound 2u (Table 8). To a 50 round-bottomed flask containing a mixture of ice cold 40 % aqueous ammonia (50 mL) and diethyl ether (50 mL), (bicyclo[2.2.1]hept-5-en-2-yl)dichloro(methyl)silane (10 mmol) was added dropwise with constant stirring. After complete addition of chlorosilane, the reaction mixture was allowed to stir under ice-cold condition. After 4 h, the organic layer was collected and dried over Na_2SO_4. On evaporation of solvent, the crude product was obtained as a white solid. Crystallization of the solid from hot $CHCl_3$ yielded (0.7g, 41%) crystalline **2u**. ^{1}HNMR ($CDCl_3$, 200 MHz): 0.36 (m, 3H), 1.07-2.15 (m, 5H), 2.90-2.19 (m, 2H), 3.90 (s, 2H), 6.20 (s, 2H).. ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) -0.3.

Compound 2v (Table 8). To a 50 round-bottomed flask containing a mixture of 40 % aqueous ammonia (50 mL) and diethyl ether (50mL), phenylvinyldichlorosilane (10 mmol) was added dropwise under ice-cold condition. After complete addition of chlorosilane, the reaction mixture was allowed to stir under ice-cold condition. After 4 h, the organic layer was collected and dried over Na_2SO_4. On evaporation of solvent, the crude product was obtained as white solid. Crystallization of the solid from hot $CHCl_3$ yielded (0.6g, 36%) crystalline **2v**. ^{1}HNMR ($CDCl_3$, 200 MHz): 3.41 (s, 2H), 5.93 (m, 1H), 6.10 (m, 2H), 7.35 (m, 3H), 7.61 (m, 2H).

3.5.2. Characterization data of organosilanols (2a-2s)

Dimethylphenylsilanol (**2a**, Table 1) ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.18 (s, 6H), 2.47 (s, 1H), 7.18 (m, 3H), 7.39 (m, 2H); ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm)-0.1,

127.8, 129.6, 133.7, 139.0; ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) 6.9; IR (neat): cm^{-1} 3312 (br), 2962, 1425, 1256.

Ethyldimethylsilanol (**2b**, Table 1) ^{1}HNMR ($CDCl_3$, 200 MHz): δ ppm) -0.74 (s, 6H), 0.39 (q, 2H, *J*=7.8 Hz), 0.78 (t, 3H, *J*=7.8 Hz). 3.31(s, 1H);^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm) -1.1, 6.5, 9.3; ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) 16.9; IR (neat): cm^{-1} 3455 (br), 2962, 1204.

***tert*-Butyldimethylsilanol** (**2c**, Table 1).^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) -0.02 (s, 6H), 0.81 (s, 9H), 3.8 (s, 1H); ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm) -3.7, 17.9, 25.6. ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) 19.0.

Triethylsilanol (**2d**, Table 1) ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.55 (q, 6H), 0.93 (t, 9H), 2.33 (s, 1H); ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm) 5.7, 6.5; ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) 19.5.

Diphenylmethylsilanol (**2e**, Table 1) ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.67 (s, 3H), 3.4 (s, 1H), 7.38 (m, 6H), 7.63 (m, 4H); ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm) -1.4, 127.8, 129.7, 133.9, 136.9; ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) -4.0. IR (neat): cm^{-1} 3281 (br), 3069, 2952, 1586, 1486, 1426, 1252, 1117.

Triphenylsilanol (**2f**, Table 1) ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 2.70 (s, 3H), 7.41 (m, 9H), 7.64(m, 6H); ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm) 127.9, 130.1, 134.9; ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) -14.0. IR (neat): cm^{-1} 3269 (br), 3060, 1587, 1482, 1426, 1117; MS (EI) 276 (90), 199 (100) 122 (31), 77 (42), 51 (28).

Diethylsilanediol (**2g**, Table 1) ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.54 (q, 4H), 0.91 (t, 6H), 2.83(s, 2H); ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm) 5.6, 6.4; ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) 18.3.

Diphenylsilanediol (**2h**, Table 1) ^{1}HNMR ($CDCl_3$, 600 MHz): δ (ppm) 2.79 (s, 1H), 7.40-7.46 (m, 3H), 7.73(m, 2H); ^{13}CNMR (THF-d_5, 200 MHz): δ (ppm) 127.7, 129.6, 134.8, 138.4; ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) -29.73.

Phenylsilanetriol (**2i**, Table 1)) ^{1}HNMR (THF-d_5, 600 MHz): δ (ppm) 5.53 (s, 3H), 7.26 (m, 3H), 7.7.68 (m, 2H). ^{13}CNMR (THF-d_5, 200 MHz): δ (ppm) 127.8, 129.6, 135.2, 138.1.; ^{29}SiNMR (THF-d_5, 600 MHz): δ (ppm) -49.3.

(*E*)-Dimethyl(2-phenylethenyl)silanol (**2j**, Table 3) ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.29 (s, 6H), 2.03 (s, 1H), 6.43 (d, 1H), 7.0 (d, 1H), 7.36 (m, 3H), 7.42 (m, 2H); ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.8, 127.7, 128.3, 129.2, 133.0, 135.8, 139.9.

(*E*)-Dimethyl[2-(trimethylsilyl)phenylethenyl)silanol (**2k**, Table 3) ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) –0.19 (s, 9H), 0.18 (s, 6H), 2.2 (s, 1H), 6.45 (s, 1H), 7.08-7.45 (m, 5H); ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm) -0.7, 0.0, 126.0, 126.4, 127.4, 127.9, 145.2, 165.1; ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) –9.1, 3.9.

Compound 2l (Table 3). ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.05(s, 18H), 0.22 (s, 6H), 3.11 (s, 1H), 6.67 (s, 1H); ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm) -1.2, -1.1, -0.2, 94.9, 106.6, 139.5, 156.6; ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) 3.4 (-*Si*Me_2OH), -7.8 (-*Si*Me_3), -18.3 (-*Si*Me_3).

Compound 2m (Table 3**).** ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.19(s, 9H), 0.24 (s, 9H), 0.56 (s, 6H), 2.94 (s, 1H), 6.8 (s, 1H), 7.39 (m, 3H), 7.67 (m, 2H); ^{29}SiNMR

($CDCl_3$, 600 MHz): δ (ppm) –8.5 (-*Si*Me_3), -19.2 (-*Si*Me_3), -20.5(-*Si*PhMeOH); MS (EI) 332 (14), 331(22), 315 (317 (39) 259 (31), 77 (42), 51 (28).

((1*E*)-2-cyclohexenylvinyl)dimethylsilanol (**2n**, Table 3) ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.11(s, 6H), 1.52 (m, 4H), 2.03 (m, 4H), 3.00 (s, 1H), 5.57 (d, 1H, *J*=18.8 Hz), 5.75 (m, 1H), 6.52 (d, *J*=18.8 Hz); ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.1, 22.4, 22.5, 23.9, 26.0, 122.6, 132.1, 137.2, 148.8; ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) 6.9 (-*Si*Me_2OH). IR (neat): cm^{-1} 3413 (br), 2934, 2865, 1704, 1578, 1439, and 1252.

1,4-bis(dimethylsilylhydroxy)benzene (**2o,** Table 4) ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.40(s, 12H), 2.10 (1s, 2H), 7.50 (s, 1H); ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm) -0.1, 132.5, 140. ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) –7.04.

Compound 2p (Table 4). ^{1}HNMR ($CDCl_3$, 200 MHz): 0.18 (s, 12H), 1.94 (s, 2H), 6.34 (d, 2H, *J*=19.2 Hz), 6.87 (d, 2H, *J*=19.2 Hz), 7.28 (s, 4H).

Compound 2q (Table 4). ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) -0.17(s, 18H), 0.13 (1s, 12H), 2.30 (s, 2H), 6.43 (s, 2H), 6.90 (s, 4H).; ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) –10.2, 3.0.

Compound 2r (Table 4). ^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) -0.15(s, 18H), 0.15 (1s, 12H), 1.92 (s, 2H), 6.40 (s, 2H), 6.73 (s, 1H), 6.82 (d, 2H, *J*= 8.0 Hz), 7.18 (d, 1H, *J*= 8.0 Hz); ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) –10.1, 2.9.

Compound 2s (Table 4). 3.04 (s, 2H), 6.71 (d, 2H, *J*= 18.8 Hz)), 7.1 (d, 2H, *J*= 18.8 Hz), 7.2-7.60 (m, 19H).

Polymer I (Scheme 3). ^{1}HNMR ($CDCl_3$, 200 MHz): 0.25 (s, 12H), 0.32 (s, 12H), 6.43 (d, 2H, *J*=12.8 Hz), 6.93 (d, 2H, *J*=12.8 Hz), 7.38 (s, 4H). 7.53 (s, 4H).); ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) –1.5, -0.8.

Polymer II (Table 8). ^{1}HNMR ($CDCl_3$, 200 MHz): -0.25 (m, 18H), -0.01 (m, 12H), 2.22 (m, 12H), 6.33 (m, 2H), 6.78 (m, 4H), 7.45 (m, 4H). ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) –9.3, -4.8. –1.1.

Polymer III (Table 8). ^{1}HNMR ($CDCl_3$, 200 MHz): -0.25 (m, 18H), -0.44 (s, 12H), 6.55 (d, 2H, *J*=14.0 Hz), 7.19 ((d, 2H, *J*=14.0 Hz), 7.54 (m, 10H), 7.85 (m, 4H).; ^{13}CNMR ($CDCl_3$, 200 MHz): δ (ppm) 4.3, 130.1, 131.0, 131.99, 132.9, 133.5, 137.7, 141.4, 147.3.; ^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) 4.28 (br).

Polymer IV (Table 8). ^{1}HNMR ($CDCl_3$, 200 MHz): 0.15 (m, 3H), 0.42 (s, 12H), 1.10-1.80 (m, 5H), 2.86-2.99 (m, 2H), 5.97 (s, 2H), 7.63 (s, 4H).

Polymer V (Table 8). ^{1}HNMR ($CDCl_3$, 200 MHz): 0.42 (m, 12H), 6.09 (m, 1H), 7.32 (m, 3H), 7.43 (m, 2H), 7.62 (m, 4H).

3.6. References

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Chapter 4

Synthesis and Morphological studies of Ferrocene-Grafted Polybutadiene

4. Introduction

For the last two decades, organometallic materials have become an exciting topic of scientific research due to their intrinsic properties (magnetic, electrical and optical) and also their use as precursors in advanced nanostructured ceramics. The wide range of applicability of these materials includes nonlinear optical devices,[1] light emitting diodes,[2] molecular magnets,[3] electrochemical censors,[4] thin film transistors,[5] and liquid crystals.[6] In particular, organometallic polymers that contain transition metal either in the backbone or in the side chain, received a great deal of interest because of their potential to combine the electrical properties of metals with the flexibility and processability of the organic polymers.[7] Among organometallic polymers, ferrocene-containing polymers are of considerable interest from the view point of their excellent thermal, redox and spectroscopic properties.[8]

There are three architectures possible for ferrocene-containing polymers[9] (a) main-chain polymers in which there is 1,1'-substitution pattern of the spacers about the ferrocene units, (b) side-chain polymers in which metallocene unit is appended to the polymeric backbone and (c) embedded side-chain polymers, a rare subclass of the side-chain polymers in which the iron atoms forms the point of lateral attachment of the side chain to the main chain (Figure 1).

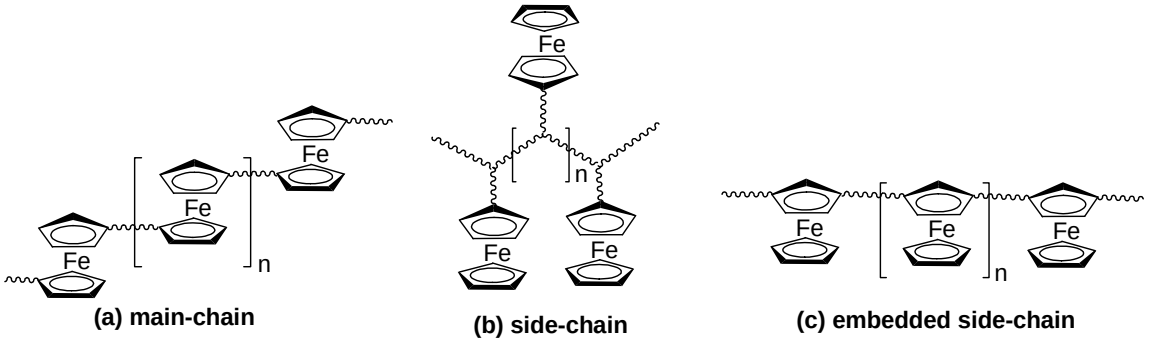
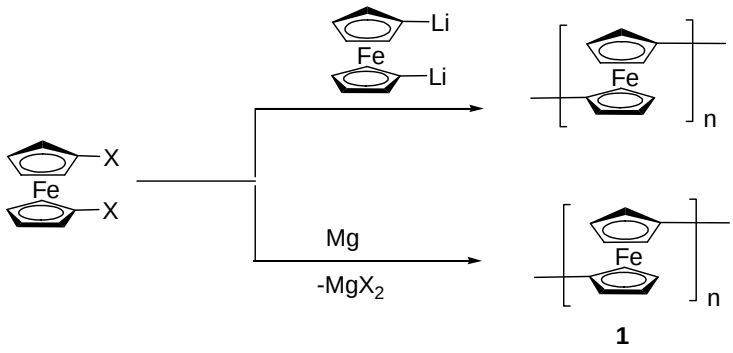


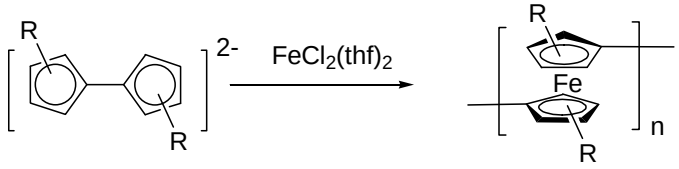
Figure 1. Three possible architectures of ferrocene-containing polymers (adopted from ref. 9)

(a) Main-Chain Ferrocene Containing Polymers: After the discovery of ferrocene molecule in 1951,[10] several attempts were made to incorporate this remarkable compound along the polymeric backbone.[11] However, incorporation of ferrocene molecules in the main-chain were not particularly successful until 1979, when Neuse has reported the synthesis of poly(ferrocenylene) **1** via step growth polycoupling reaction of equimolar amount of dilithioferrocene, tetramethylethylenediamine (TMEDA) with diiodoferrocene at room temperature (eq 1).[12] Later in the 1980s, Yamamoto and coworkers have reported dehalogenation of dihaloferrocenes in presence of magnesium, affording semicrystalline poly(ferrocenylene) (eq 1).[13]



(1)

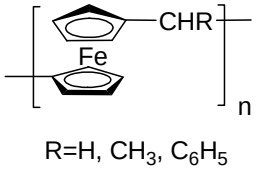
In 1996, Nishihara and coworkers have described a methodology that permits the synthesis of more soluble substituted poly(ferrocenylenes) **2** via the reaction of dihexylfulvalene dianion with $[FeCl_2(thf)_2]$ (eq 2).[14]



(2)

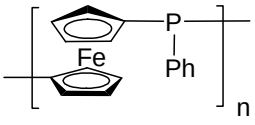
2

Poly(metallocenes) with-single carbon bridges (**3)** have been synthesized via condensation or cationic polymerization methods in presence of Lewis acid or protic acid catalysts.[15] In 1967, Neuse and Pittman have reported a similar route for phosphorous-bridged poly(ferrocenes) (**4** and **5)**.[16]

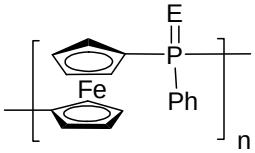


R=H, CH_3, C_6H_5

3

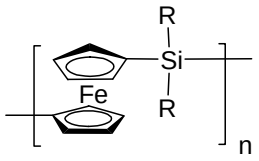


4



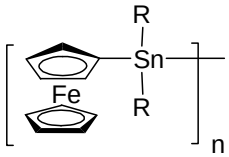
E= O, S

5



R= CH_3, C_6H_5

6



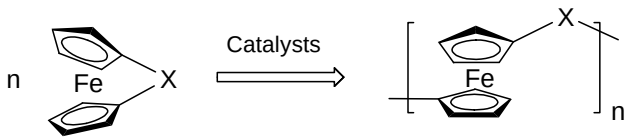
R=CH_3, C_6H_5

7

Silicon-bridged poly(ferrocenes), polyferrocenylsilanes (**6**) were first synthesized by polycondensation of dilithioferrocene with appropriate dihaloorganosilanes (Me_2SiCl_2 or Ph_2SiCl_2).[17] Following a similar pathway, Osborne and Seyferth have reported the synthesis of poly(ferrocenylstannanes) (**7**).[18] However, due to the difficulty in obtaining

dilithioferrocene reagents with high purity, the molecular weight of these polymers was extremely low.[11a]

Since the discovery in 1992 by Manners and Coworkers,[19] the ring-opening polymerization (ROP) of strained ferrocenophanes (**8**) have been in the center stage for the formation of main-chain ferrocene containing polymers.

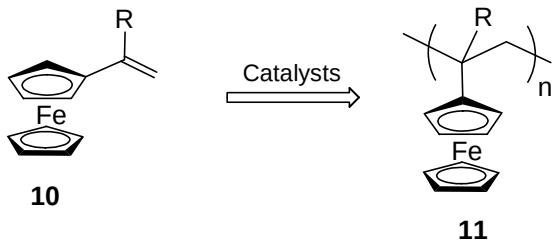


(X contains Si, Ge, Sn, P, As, S and Se) (3)

8 **9**

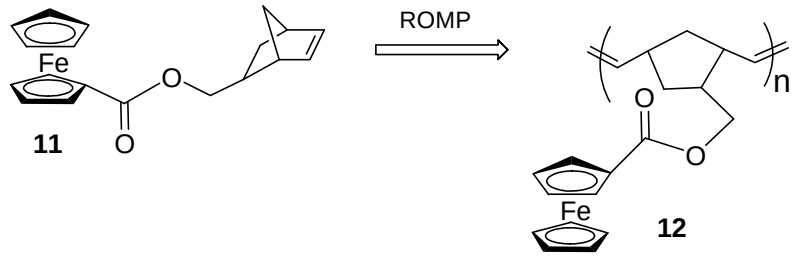
Most of the work on ROP reactions has been carried out on silaferrocenophanes and initially the substituents attached to the silicon atom were limited to aryl and alkyl groups,[20] but later silaferrocenophanes substituted with amino, alkoxy and aryloxy groups have been reported, giving access to the hydrophilic or water soluble polymers.[21] Besides these, a wide variety of polymers were also obtained via the ROP reactions of [1]ferrocenophanes containing the elements such as B, Ge, Sn, P, As, S and Se.[22]

(b) Side-Chain Ferrocene Containing Polymers: The incorporation of ferrocene into the side chain along a polymeric backbone can be achieved either by constructing the polymers from monomeric units already bearing metallocene or by post functionalization of a polymer at a later stage. In 1955, Arimoto and Haven have synthesized the first polymer bearing side-chain ferrocene units via the radical polymerization of vinylferrocene (eq. 4).[23]



10 **11** **(4)**

Generally the molecular weights of the polymers obtained by this method are less than 10,000 g/mol. Although the synthesis of polymers with high molecular weights ($Mw>10^5$) has been achieved using this method, such polymers possess multi-modal molecular weight distribution. A variety of other alkenyl-substituted ferrocenes such as acrylates, methacrylates and isopropenylferrocenes have also been successfully polymerized under similar conditions.[11b] Vinyl ferrocene has also been co-polymerized with other alkenyl compounds (eq. 4).[24a] Other than radical-initiated polymerization, cationic and Ziegler-Natta type polymerization method have also been successfully employed in order to obtain polyvinylferrocenes.[24b] Besides these classical radical polymerization methods, ring-opening metathesis polymerization (ROMP) has also been applied to synthesize side-chain ferrocenyl polymers (eq. 5). For example, Mirkin and Coworkers have used this approach to graft side-chain ferrocene polymers on gold nanoparticles.[25]



11 **12** **(5)**

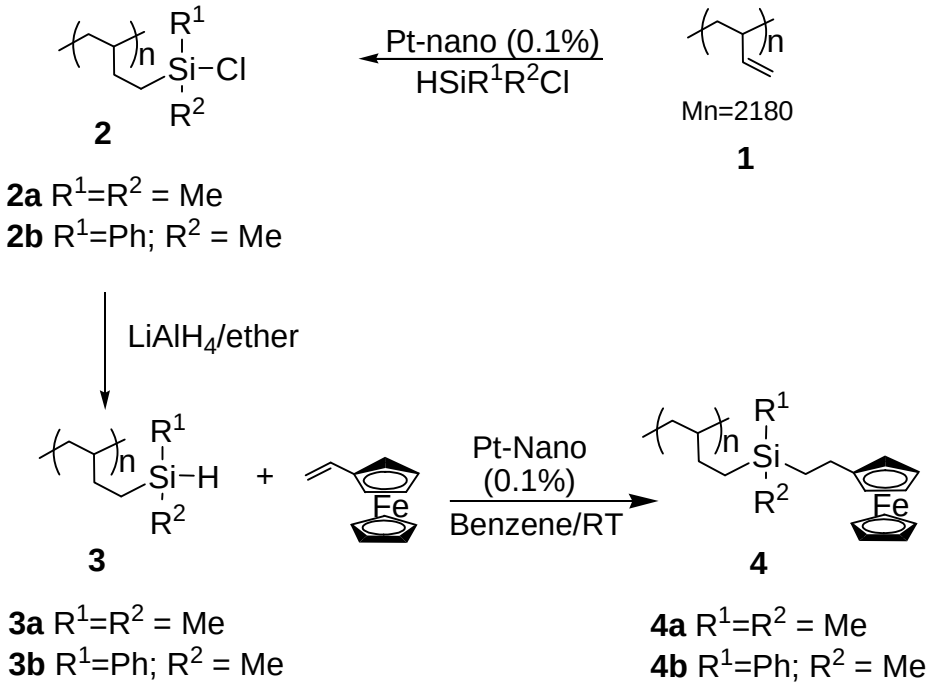
(b) Embedded Side-Chain Ferrocene Containing Polymers: This is one of the rare and least well-represented classes of the ferrocene-containing polymers, in which the ferrocene units are linked together through only one of the cyclopentadienyl rings. [26,27,28]

In our group, we are interested in the synthesis of new classes of silicon-based polymer systems having polybutadiene frame-works. Recently, we have reported a highly selective and mild synthetic route to silyl-functionalization of 1,2-polybutadienes (PBD) using Pt-nanocluster catalysis.[29] In continuation of this work, we also have developed our strategy to generate new families of organo-functional silicon polymers by grafting of various silyl-polybutadienes.[30] In this chapter, we describe the synthesis, characterization and morphological studies of new ferrocene functionalized side chain polymers, via grafting of silyl-functional polybutadienes.

4.1. Synthesis of Ferrocene-Grafted Polybutadiene

Our strategy to synthesize ferrocene-grafted polybutadiene involves a three-step process (Scheme 1). (a) Hydrosilylation of polybutadiene with a chloro-substituted hydrosilanes to obtain chlorosilylated polybutadiene (PBD-SiCl). (b) Reduction of the chlorosilylated-polybutadiene to corresponding hydrosilylated-polybutadiene (PBD-SiH) and (b) The attachment of vinylferrocene molecules to this PBD-SiH via hydrosilylation reaction.

Scheme 1. Synthesis of ferrocenyl-grafted polybutadiene via hydrosilylation.



The PBD-SiCl **2**, has been synthesized using our previously established hydrosilylation of 1,2-polybutadine using Pt-nanoclusters as catalysts.[30] The reduction of this PBD-SiCl using $LiAlH_4$ (LAH) afforded the polymers with pendant Si-H group, (PBD-SiH, **3**). The PBD-SiH thus obtained was further grafted with vinylferrocene via Pt-nanoclusters catalyzed hydrosilylation reaction to obtain side-chain ferrocene-functional polybutadiene. The polymer products obtained were further characterized by using GPC, ^{1}H NMR, ^{13}C NMR ^{29}Si NMR, FTIR, TG-DTA and DSC techniques.

^{1}H and ^{13}C NMR studies of the products suggested that the hydrosilylation of PBD **1**, occurs selectively via an anti-Markovnikov addition i.e., the Si atom being attached at the terminal position of the olefin bond (β-product) (Figure 2). Distortionless Enhancement by Polarization Transfer (DEPT) of ^{13}C NMR was used to identify the regioselectivity of the hydrosilylation reaction**.** The selectivity towards β-product was

verified for all the products by DEPT technique. For instance, the DEPT spectrum of **4a** has shown one upward resonance at ~33.0 which can be assigned to the methine carbon (CH) and three downward signals in region of 10, 26 and 37, are attributed to the three methylene (CH_2) carbons of polymer backbone of β-product (Figure 3). The opposite regioselectivity (α) would have generated three upward (two CH and one CH_3 carbons) and one downward signals (CH_2), lacking of which clearly indicates the exclusive formation of β-product. Formation of single product has also been supported by appearance of single peak in their ^{29}Si NMR (Figure 4).

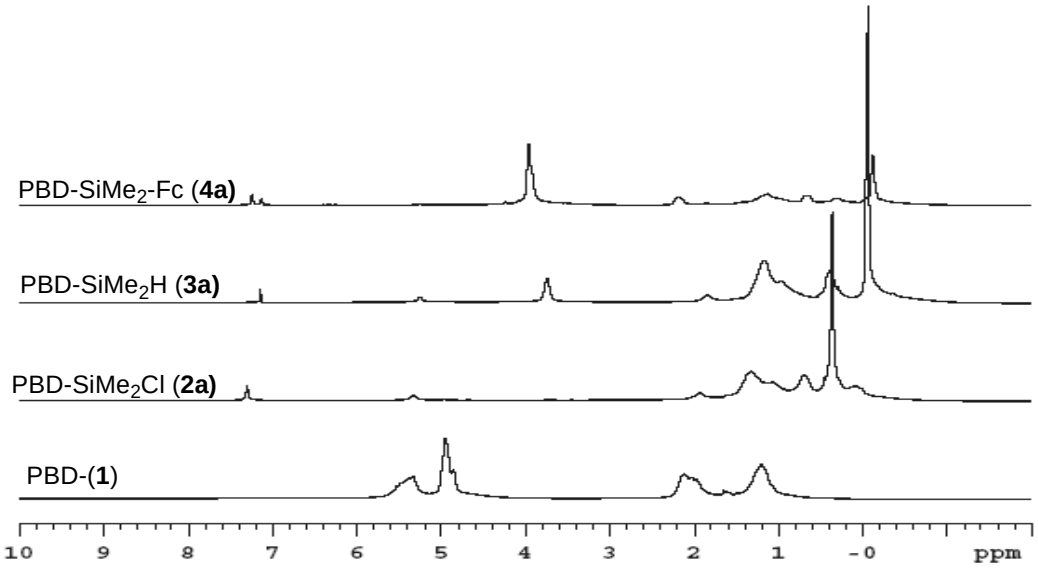


Figure 2. ^1H NMR of PBD-1, PBD-$SiMe_2Cl$ (**2a**), PBD-$SiMe_2H$ (**3a**) and PBD-$SiMe_2$-Fc (**4a**).

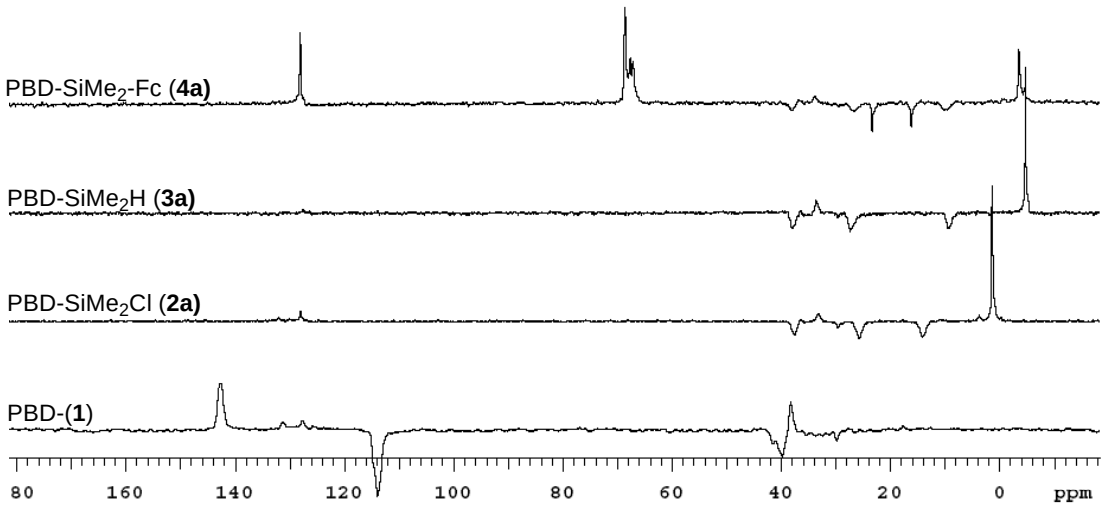


Figure 3. ^{13}C NMR (DEPT) analysis PBD-**1**, PBD-$SiMe_2Cl$ (**2a**), PBD-$SiMe_2H$ (**3a**) and PBD-$SiMe_2$-Fc (**4a**).

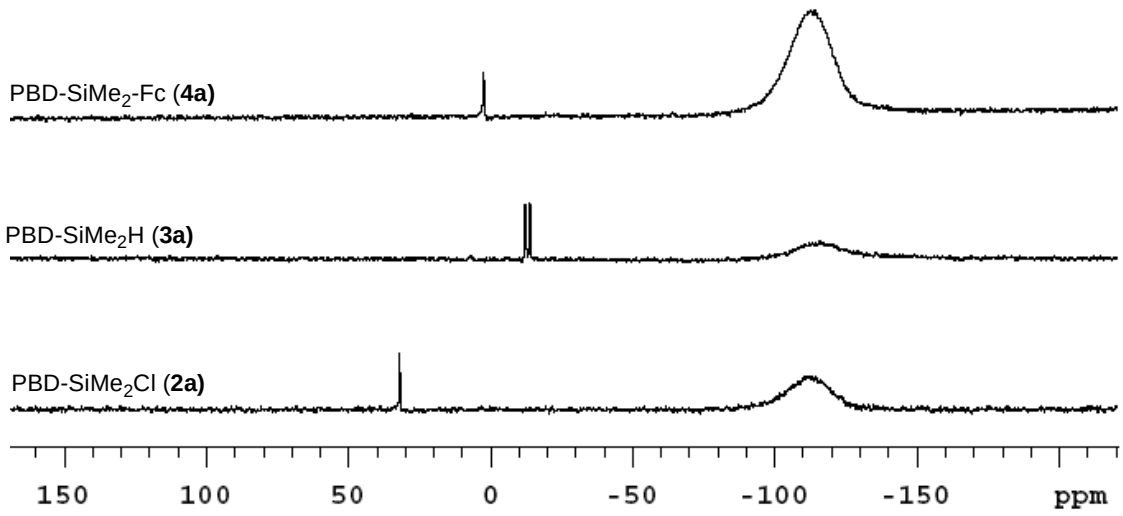


Figure 4. ^{29}Si NMR analysis PBD-$SiMe_2Cl$ (**2a**), PBD-$SiMe_2H$ (**3a**) and PBD-$SiMe_2$-Fc (**4a**).

The molecular weights and the chain length properties of the synthesized polymers have been studied by Gel Permeation Chromatography (GPC) using

polystyrene standards as reference. The GPC chromatograms of all polymers with THF as an eluent were found to be monomodal, and they have clearly shifted towards the high molecular weight region, while retaining their molecular weight distributions (M_w/M_n) in the range of ~1.5-1.7, closer to the value obtained for pure polybutadiene (Figure 5). This analysis confirmed that no other side reactions such as chain scission, cross-linking, etc. occurred during the course of the hydrosilylation reaction, leaving large-scale molecular structure intact.

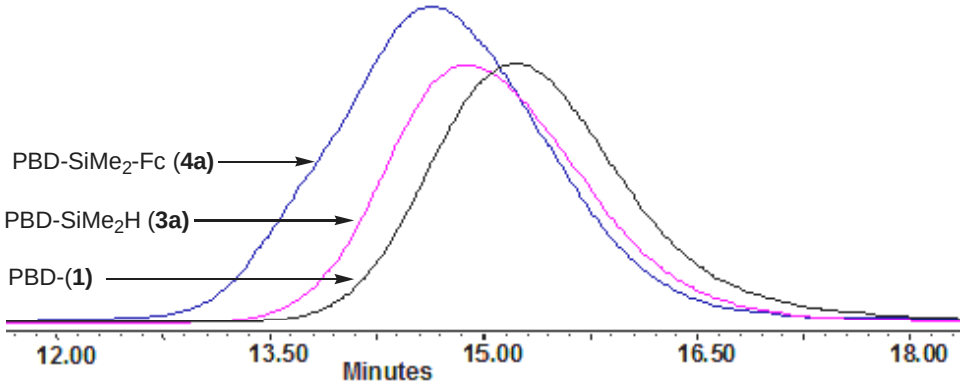
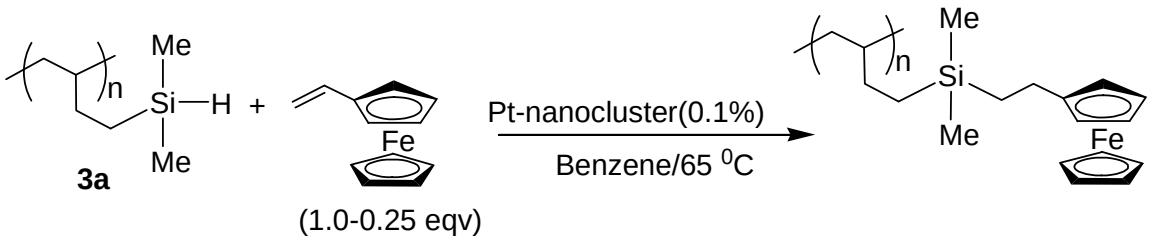


Figure 5. GPC of polymers PBD-**1**, **3a and 4a.**

To find the scope and limitation of this method, we made an attempt to synthesize the polymers with controlled ferrocene loading. Thus, under identical reaction conditions, PBD-SiH **3a** (0.115 g, 1.0 mmol) was treated with three different amounts of vinylferrocene (0.75, 0.50 and 0.25 eqv.) in the presence of Pt-nanocluster catalysts (Scheme 2).

Scheme 2. Controlled ferrocene loading on silyl-functional polybutadiene (**3a**)



4a = 1.00 eqv Fe
5a= 0.75 eqv Fe
6a= 0.50 eqv Fe
7a= 0.25 eqv Fe

The analysis of the products using NMR, FTIR and GPC showed quantitative incorporation of vinylferrocene in polymer **3a** without any side reactions associated with unreacted Si-H. Polymer **3a** shows a doublet peak at δ= -12 ppm in the ^{29}Si NMR originating from silicon atom of *Si*Me_2H moiety, whereas polymer **4a** shows a single peak at δ= 8.0 ppm corresponding to the substituted silicon atom. In case of polymers **5a**, **6a** and **7a,** along with the peak at δ= 8.0 ppm, the gradual increase in intensity of doublet peak (δ= -12.0 ppm, corresponding to *Si*Me_2H) was observed, with decreasing amount of ferrocene content (Figure 6). FTIR observation of three polymers **5a, 6a, 7a** having unreacted Si-H has also revealed similar trend (Figure 7).

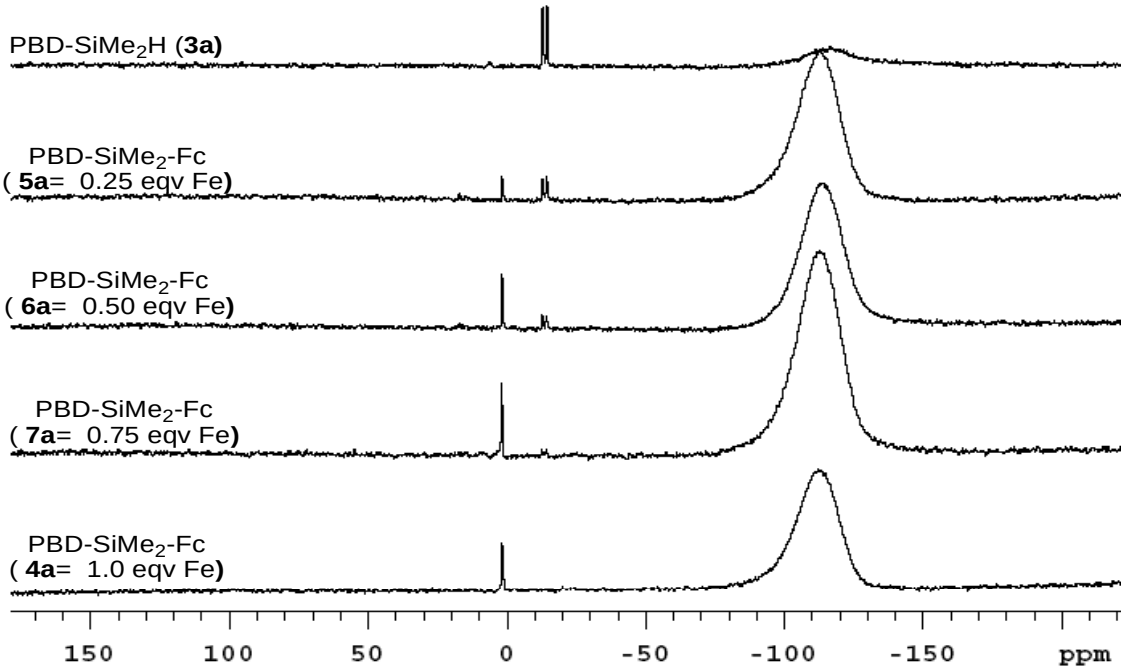


Figure 6. ^{29}Si NMR of polymer **4a**, **5a**, **6a** and **7a**.

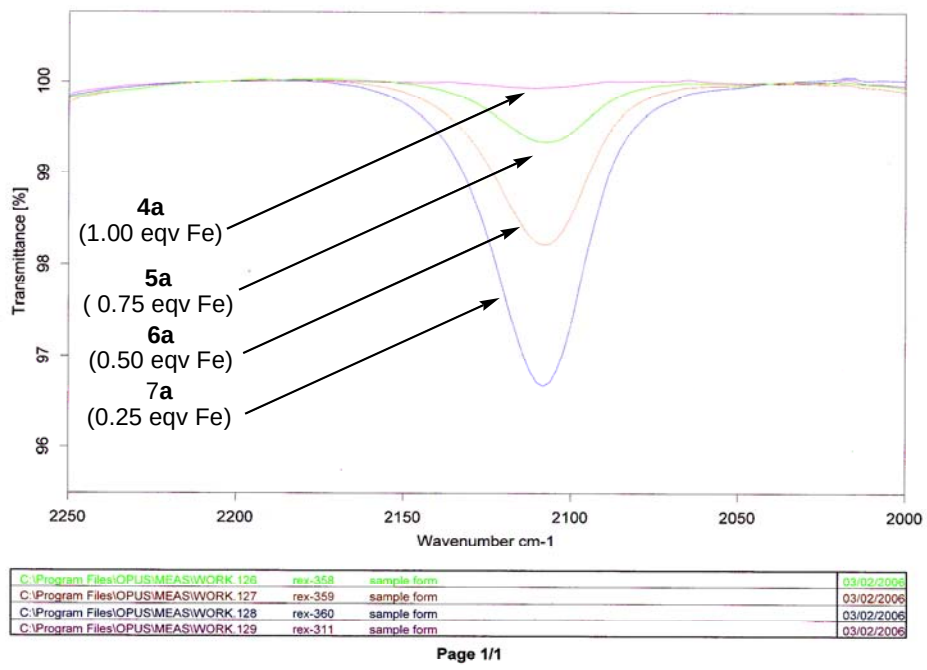


Figure 7. FTIR spectra of polymer **4a**, **5a**, **6a** and **7a** (Si-H Stretching frequency).

4.2.1. Thermogravimetric Analysis

The thermal stability of the polymer PBD and **5a** was evaluated by TG-DTA under nitrogen atmosphere. Thermo gravimetric curves of both the polymers showed a good thermal stability with the starting temperature of weight loss at ~370 °C and a subsequent rapid weight loss observed at ~400°C. Almost complete thermal decomposition (100%) was observed at ~480°C for pure PBD where as a weight loss of only 88% was observed (at ~480°C) for **4a**, which corresponds to decomposition of backbone polymer (Figure 8). The differential scanning calorimetry (DSC) technique allowed the observation of glass transition temperature (T_g) for the PBD and **4a** (Figure 9). These polymers exhibit a significant glass transition temperature at -25°C for PBD polymer and at 0.1°C for **4a**. A significant increase in T_g temperature (~25 °C) was observed upon the substitution of ferrocenyl groups on polybutadiene backbone.

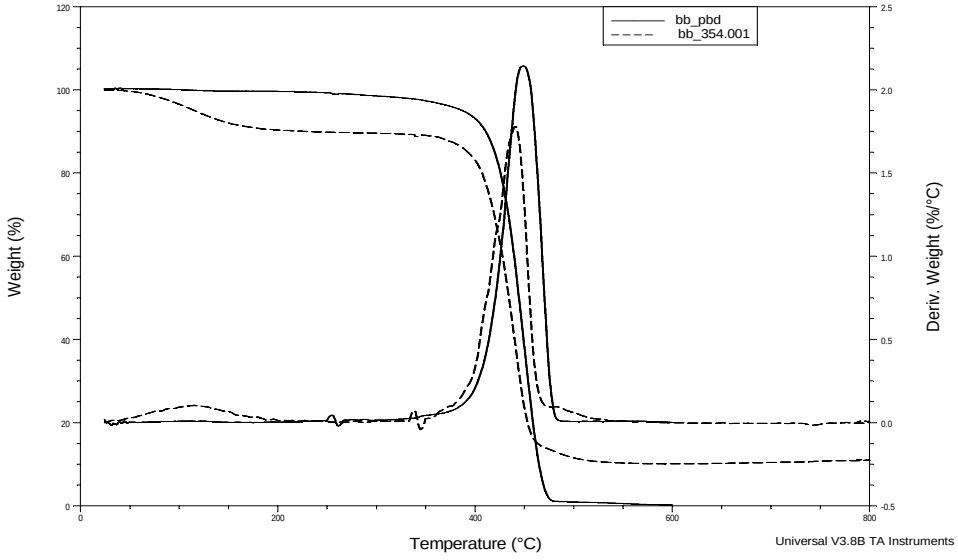


Figure 8. TGA-DTA curves of PBD and **4a**.

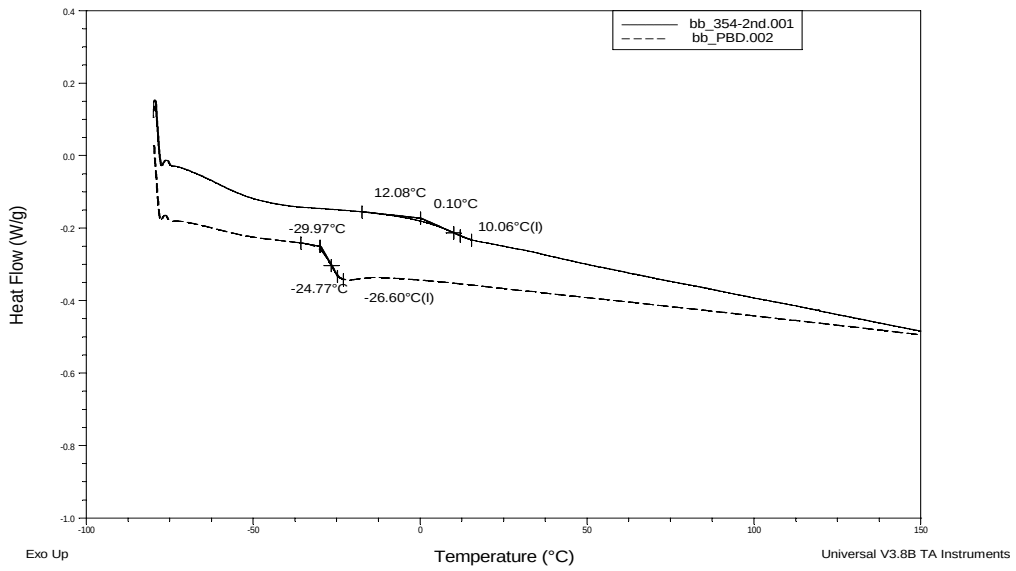


Figure 9. DSC curves of PBD and **4a**

4.2.2. Morphological Characterization

The self-assembly of hybrid organic-organometallic block copolymers in selective solvents is attracting much interest due to the variety of nanoscale structures that can be obtained and the potentially useful properties of the assemblies.[31] For example diblock copolymers of PFS with polyisoprene (PI-b-PFDMS) with a long PI block form dense wormlike micells in hexane and decane.[32] In another case, when the soluble block is poly(dimethylsiloxane) (PDMS), the type of structure formed depends on the relative lengths of the PFDMS and PDMS blocks. For example $PFDMS_{50}$-$PDMS_{300}$ forms cylindrical (wormlike) micelles in hexane, [33] but when the ratio of PDMS to PFDMS is increased, long hollow structures are formed.[34] It has been proposed that crystallization of the core polymer PFDMS is the driving force for the formation of the cylindrical micelles.[32]

The morphology of polymer **4a** was studied using AFM, TEM and SEM techniques. The films for tapping mode AFM and SEM were made by spin casting of one drop of polymer solution (0.005 mg/mL in THF) onto a clean silicon wafer and air drying for 24 h. The AFM picture as shown in Figure 10 has revealed the formation of spherical nanostructures. To verify the morphology, the same silicon wafer surface was analyzed by scanning electron microscope (SEM), which has shown similar spherical morphology (Figure 11). The diameter of the spherical nanostructures obtained from AFM and SEM analysis were found to be in the region of 60-100 nm. The morphology of polymer **4a** was also studied by transmission electron microscope (TEM). The TEM images showed the morphology of spherical structures with a nominal diameter in the range of 80-100 nm (Figure 12).

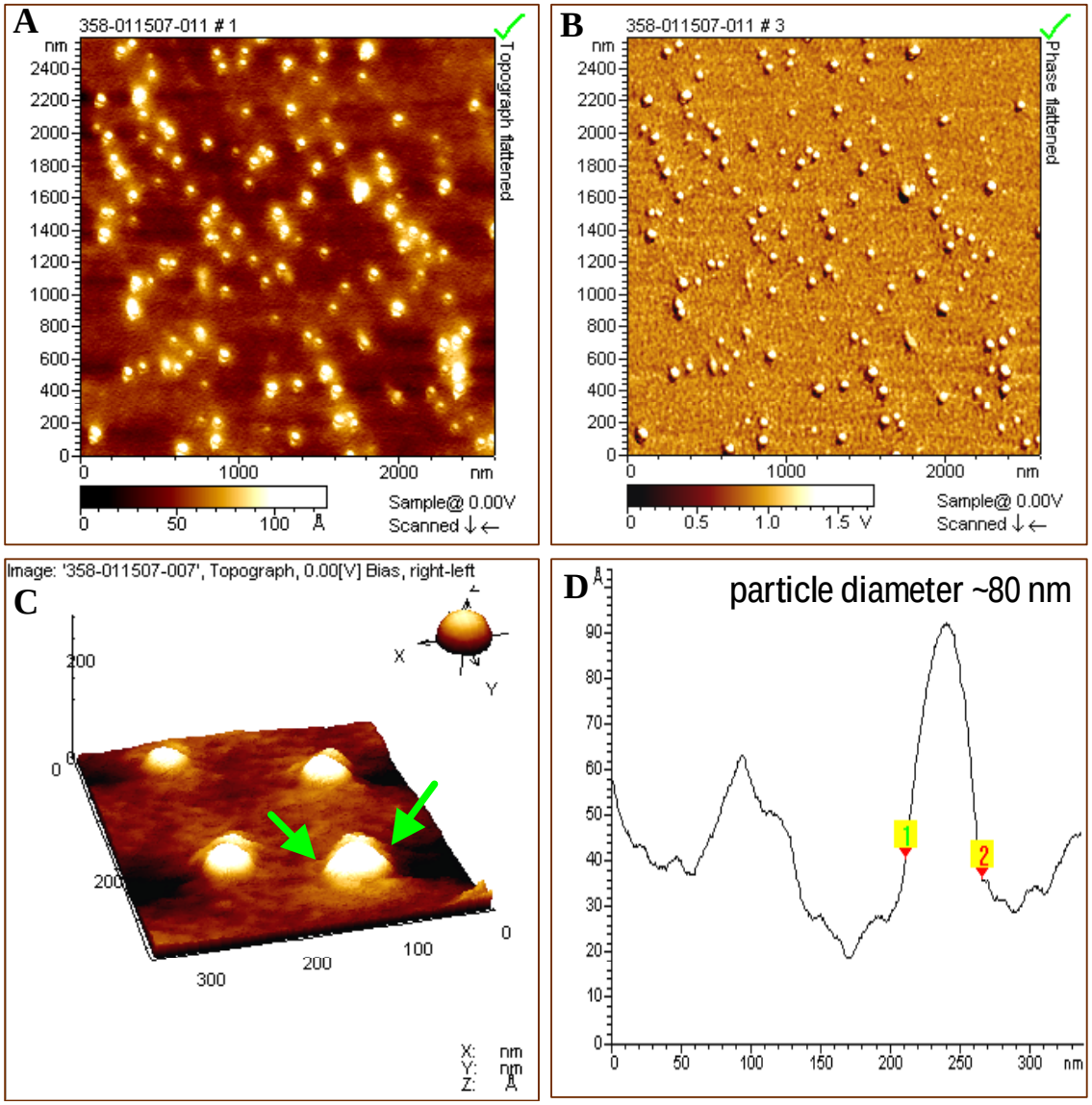


Figure 10. AFM analysis polymer **4a**, (A) Topography (B) Phase flattened (C) 3D and (D) Particle size.

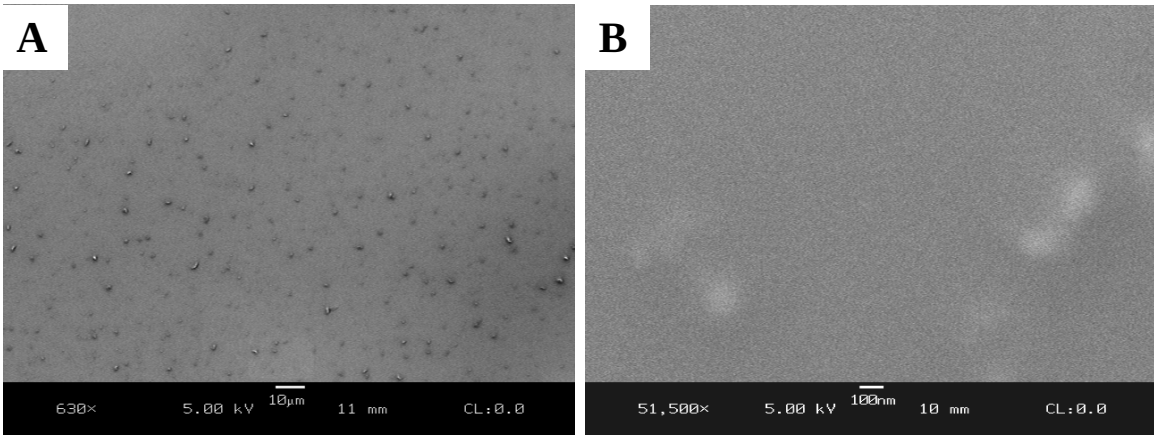


Figure 11. SEM analysis polymer **4a.**

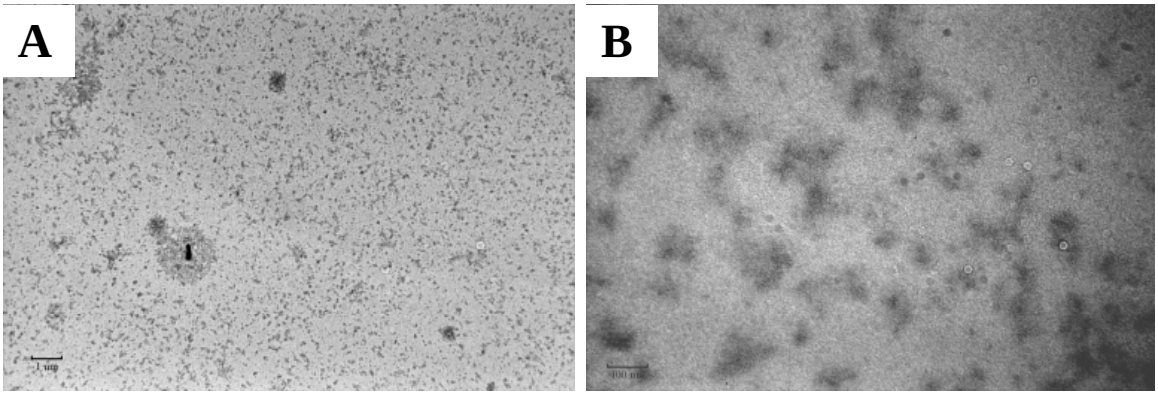


Figure 12. TEM analysis polymer **4a.**

The morphology of other three side chain polymers with three different ferrocene contents **5a**, **6a** and **7a** were also studied by AFM. The AFM studies reveal the similar spherical nanostructures as represented in Figure 13A, 13B and 13C.

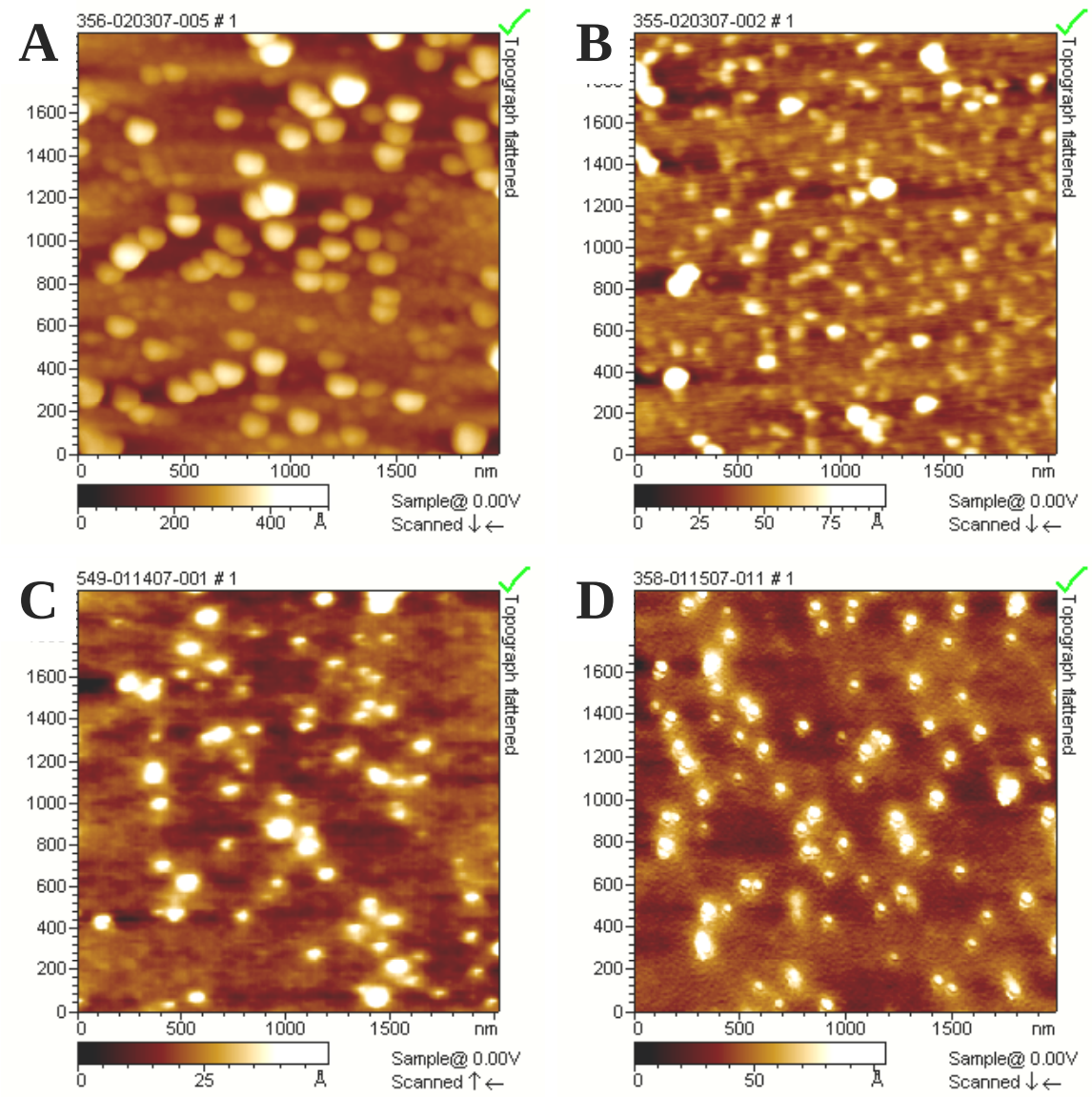


Figure 13. AFM topographic images of polymers with different ferrocene contents (A) **7a**, (B) **6a**, (C) **5a** and (D) **4a**.

4.2.3. Pyrolysis of ferrocene-grafted polybutadienes

In the past few decades, there has been increasing interest in the synthesis of ceramic materials from polymeric precursors.[35] This aproach of synthesizing ceramic materials can offer several advantages over conventional ceramic synthesis, such as low processing temperature, control of ceramic composition and microstructure. Recently, ferrocene-containing organosilicon polymers have been used as pyrolytic precursors to generate shaped-ceramics with tunable magetic properties.[36] In order to investigate the ceramic properties of our newly synthesized ferrocene functionalized polybutadiene we have pyrolyzed the polymer sample (**4a**) and studied its morphological and magnetic properties. In an experimental procedure, solution of polymer **4a** (0.005 mg/mL) was deposited by spin coating onto a silicon-surface and heated above 600 ^{0}C. The residue remaining after pyrolysis was analyzed by AFM. The AFM studies showed the retention of spherical shape with the diameter in the range of ~ 80-100 nm (Figure 14).

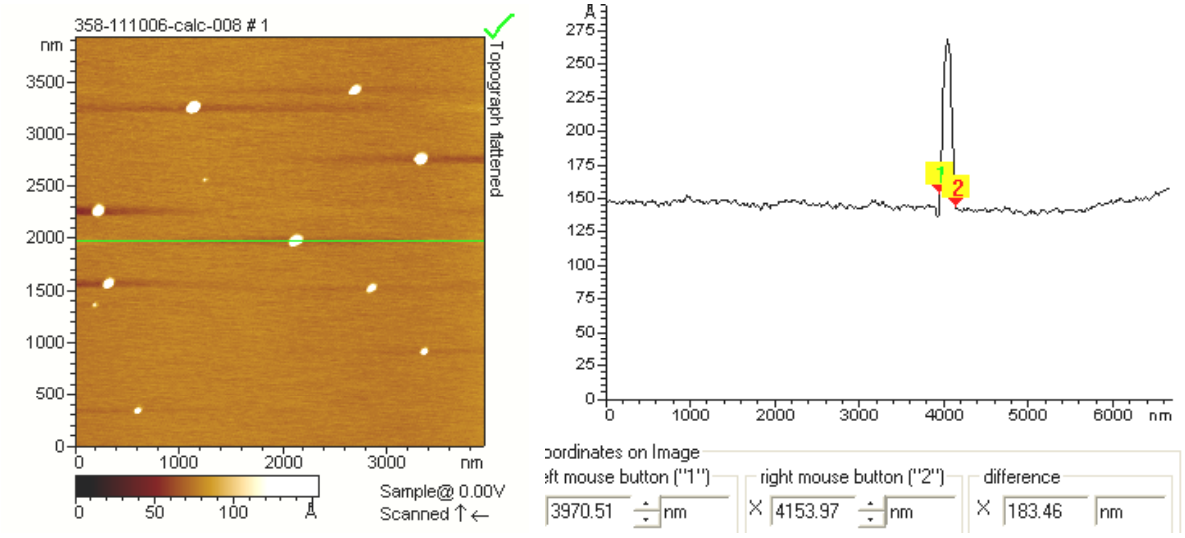


Figure 14. AFM topographic image of pyrolyzed residue obtained from polymer **4a**.

In another experiment to study the surface property of the pyrolyzed product in a bulk, polymer **4a** (0.50 g) was heated at 600 ^{0}C under N_2 for 10 min. when a black magnetically active solid (0.06 g, 12%) was obtained. The scanning electron microscopy (SEM) of the bulk solid revealed the presence of spherical particles (~100 nm) with uniform distribution (Figure 15A and 15B). The energy dispersive X-ray EDX analysis revealed the composition of the surface of this ceramic material as iron (14% wt), silicon (21% wt) and oxygen (64% wt) (Figure 15C).

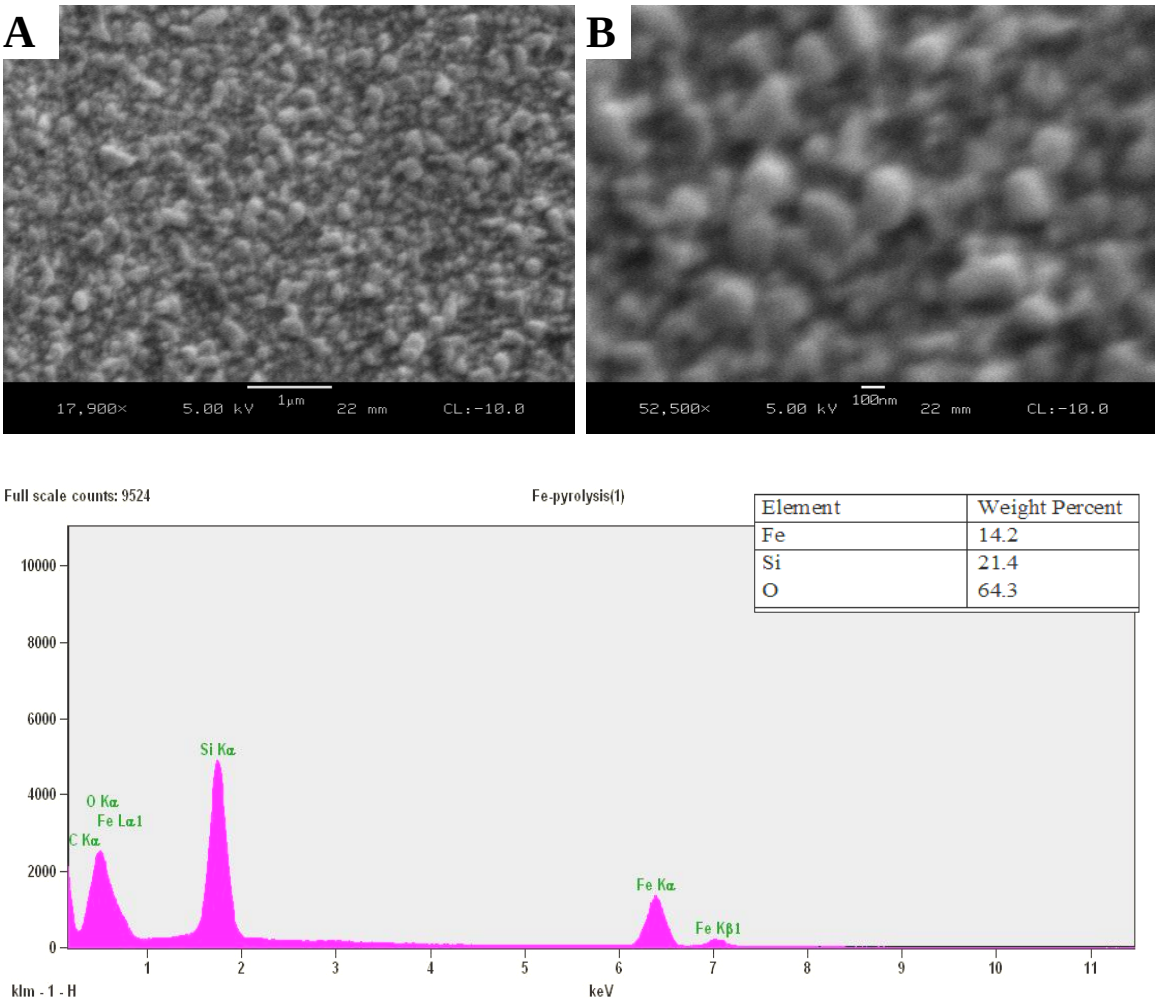


Figure 15. SEM and EDX analysis of the residue obtained via pyrolysis of **4a.**

4.2.4. Cyclic Voltametric Experiment

The solution electrochemical behavior of **4a** was analyzed via cyclic voltammetry using THF solution with 0.1M TBAF (tetra butyl ammonium fluoride) and platinum electrode. The polymer exhibits a single reversible oxidation process with $E_{1/2}$ value of 0.45 eV (Figure 16). The detection of single reversible oxidation waves indicates that in these polymers, the iron centers are essentially noninteracting. [37]

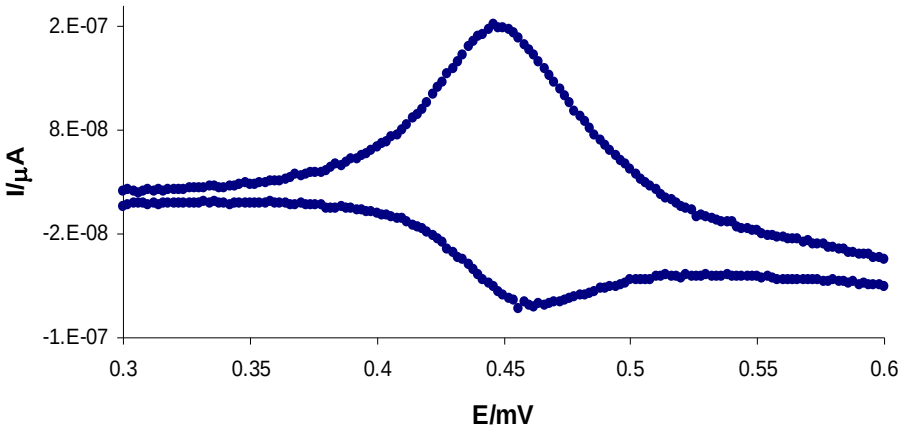


Figure 16. Cyclic voltametric analysis of polymer **4a**.

4.3. Conclusion

A new ferrocene functionalized organo-silicon polymer has been synthesized using Pt-nanocluster catalysis. The metallocene unit has been incorporated into the polymer backbone as a side chain via hydrosilylation reaction of vinylferrocene The structure and regioselectivity of new ferrocene based polymers were determined using multinuclear NMR techniques such as ^{1}H, ^{13}C and ^{29}Si NMR. The high regioselectivity (anti-Markovnikov's product) of these polymer products was confirmed by Distortionless Enhancement Polarization Transfer (DEPT) technique. The differential scanning calorimetric analysis (DSC) revealed significant increase in the glass transition

temperature after functionalization with ferrocene. The morphological analysis using AFM, SEM and TEM has revealed the self-assembling of these ferrocene-grafted polybutadiene into spherical nanostructures.

4.4. Experimental Section

General Information. All of the experiments and manipulations were performed under dry oxygen-free nitrogen using standard Schlenk-line techniques. All the solvents were purchased from EM science (Merck) and distilled over sodium/benzophenone before use. PMHS (Mw ≈ 2000), $Me_2Pt(COD)$, polybutadienes and silanes were purchased from Aldrich Chemical Co., and Gelest Chemical Co. and used without further purification. ^{1}H NMR, ^{13}C NMR and ^{29}Si NMR spectra were recorded on 200 MHz and 600 MHz Varian Unity NMR instruments with $CDCl_3$ as an internal standard. GPC analysis was carried out on Alliance GPCV 200 (Water) instrument, equipped with two silica columns, HRSE and HR-1 with the pore size range of 100-5000 Å and 2000-4x10^6 Å respectively. This instrument was calibrated using polystyrene standards. THF was used as an eluent at the flow rate of 1mL/min at 40 ^{0}C. A third order calibration curve was used to measure the molecular weight of unknown samples**.** Philips CM 100 transmission electron microscope (TEM) was employed to examine the reaction mixture for the presence of Pt-nanoclusters. Scanning electron microscope Amray 1910 (SEM) was used to analyze solid Pt-nanocluster. Thermogravimetric analysis (TGA) of functional polymers was carried out in a TGA 2950 thermogravimetric analyzer, TA Instruments, in the range of 25-800 ºC at scanning rate of 10ºC /min, under nitrogen flow. Differential scanning calorimetry, DSC, was undertaken using TA instruments, DSCQ100 model. Samples

were run in the temperature range between –80 ºC to 200 ºC , under nitrogen flow, at a scanning rate of 10ºC/min.

Typical Procedure For the synthesis of Ferrocene Functional Polybutadiene.

Step 1: In a typical procedure, a Schlenk tube (10 mL), equipped with magnetic stirrer and oil bath was charged with Pt-nanoclusters (0.01g, 0.001 mmol Pt), degassed and flushed with dry nitrogen. The PBD-**1** (0.104 g, 2 mmol) dissolved in dry benzene (2 mL) was added to the Schlenk tube followed by the addition of $HSiMe_2Cl$ (0.26 mL, 2.4 mmol) under constant flow of nitrogen. After a few minutes of stirring, the reaction mixture turned into light brown homogeneous solution, indicating the formation of soluble nanoclusters.[12] The reaction progress was monitored by ^1H NMR spectroscopy. On completion of the reaction, the catalyst was separated by centrifugation (1h) and the solvent was evaporated into round-bottom flask when PBD-SiCl **2a** (0.29 g, 2.0 mmol), was obtained as yellow viscous liquid.

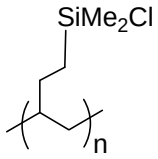
Step 2: To this viscous liquid, dry ether (50 mL) and LAH (0.12 g, 2.0 mmol) were consecutively added at 0 ^0C and the resulting mixture was allowed to stir at room temperature. After 6 h, the reaction mixture was poured in portions into ice-cold water under constant stirring. The organic layer was collected, dried over $MgSO_4$ and evaporated when PBD-SiH **3a** (0.21 g, 92%) was obtained as colorless viscous liquid. After confirming the structure using GPC/NMR, the polymer was further hydrosilylated with vinylferrocene.

Step 3: To a Schlenk tube containing Pt-nanoclusters (0.005 g, 0.001 mmol) and vinylferrocene (0.21 g, 1.0 mmol), PBD-SiH **2a** (0.112 g, 1.0 mmol) dissolved in dry benzene (2 mL) was added under nitrogen. The resulting mixture was then placed into an

oil-bath maintained at 60 ^{0}C and allowed to stir. After few minutes of stirring, the reaction mixture turned into light brown homogeneous solution, indicating the formation of soluble nanoclusters.[12] The reaction progress was monitored by ^{1}H NMR spectroscopy. After 24h, the complete disappearance of peaks corresponding to vinyl and Si-H groups in ^{1}H NMR spectra of the crude reaction mixture suggested the complete substitution of Si-H bonds with ferrocenyl groups. On completion of the reaction, the solid catalyst was separated by centrifugation (1h). The filtrate was collected and evacuated and polymer **4a** (0.31 g, 98% yield) as yellow viscous liquid.

Multinuclear NMR data of the product(s).

Polymer, 1a

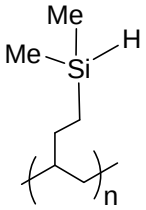


^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.07 (s, 6H), 0.0-2 (br, 7H)

^{13}CNMR/DEPT ($CDCl_3$, 200 MHz): δ (ppm) 1.62 (-Si*CH*$_3$), 14.37 (-CH_2*CH_2*Si-), 26.1(-*CH_2*CH_2Si-), 33.6(-*CH*CH_2-), 38.1 (-CH*CH_2*-).

^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) 32.97.

Polymer, 2a

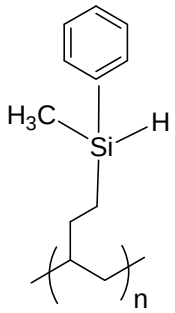


^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.04-0.06 (d, 6H), 0.38 (br, 2H), 0.6-2.0 (br, 5H), 3.74 (s, 1H)**.**

^{13}CNMR/DEPT ($CDCl_3$, 200 MHz): δ (ppm) -4.7 (-Si*CH_2*CH_3), 9.3 (-$SiCH_2$*CH_3*), 27.3 (-*CH_2*CH_2Si), 33.8 (-*CH*CH_2-), 37.9 (-CH*CH_2*-).

^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) –11.8 (d).

Polymer **2b**

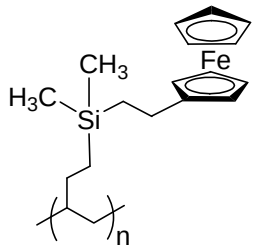


^{1}HNMR ($CDCl_3$), δ (ppm): 0.029(d, 6H), 0.35-2.0 (br,7H), 4.32 (s, 1H), 7.3 (m, 3H), 7.48 (br, 2H).

^{13}CNMR/DEPT($CDCl_3$), δ (ppm): –5.8 (Si*CH_2*CH_3), 8.6 ($SiCH_2$*CH_3*), 27.38 (*CH_2*CH_2Si), 33.6 (-*CH*CH_2-), 38.05(-CH*CH_2*), 127.62 (-C_6H_5-), 128.96 (-C_6H_5-), 133.11(-C_6H_5-), 134.05 (-C_6H_5-).

^{29}SiNMR ($CDCl_3$,600MHz), δ(ppm): -13.3 (d)

Polymer **5a**

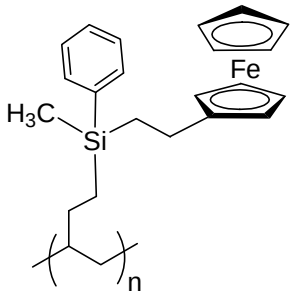


^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) -0.11 (s, 6H), 0.32(m, 2H), 0.66 (m, 2H), 0.7-2.0 (br, 5H), 2.1 (m, 2H) 3.95 (m, 9H).

^{13}CNMR/DEPT ($CDCl_3$, 200 MHz): δ (ppm) –3.5 (-Si*CH*$_3$), 9.9 (-CH_2*CH*$_2$Si-), 16.18 (-*CH*$_2$Si-), 23.36 (-*CH*$_2$-), 26.76 (-CH*CH*$_2$-), 33.71 (-*CH*CH_2-), 37.98 (-CH*CH*$_2$-), 68.0 (-C_5H_5-), 69.09 (-C_5H_5-).

^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) 2.3

Polymer **5b**



^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.24 (m, 2H), 0.4-2.2 (br, 5H), 4.03 (m, 9H), 7.35 (m, 2H), 7.46 (m, 3H).

^{13}CNMR/DEPT ($CDCl_3$, 200 MHz): δ (ppm) –4.6 (-Si*CH*$_3$), 14.55 (-CH_2*CH*$_2$Si-), 21.89 (-*CH*$_2$Si-), 25.30 (-*CH*$_2$$CH_2$Si-), 27.61 (-*CH*$_2$-$C_5H_5$-), 32.71 (-*CH*$CH_2$-), 37.98 (-CH*CH*$_2$-), 67.0 (-$C_5H_5$-), 68.09 (-$C_5H_5$-), 127.4 (-*C*$_6$*H*$_6$-), 128.6 (-*C*$_6$*H*$_6$-), 133 (-*C*$_6$*H*$_6$-), 133.64 (-*C*$_6$*H*$_6$-).

^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) –2.

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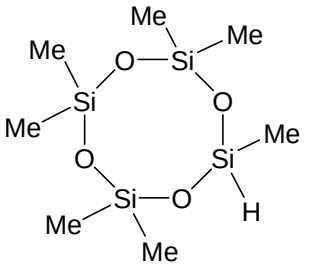
Chapter 5

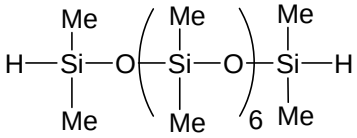
Siloxy-functional Polybutadiene: Synthesis and Characterization

5. Introduction

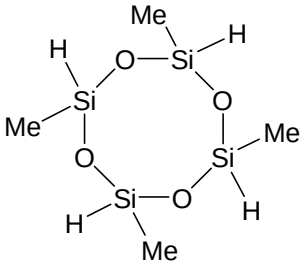
Incorporation of well-defined inorganic or organometallic building blocks into the organic polymer chains have been considered potentially attractive for the purpose of developing hybrid-materials with distinct and improved properties.[1] Cyclic siloxanes and polyhedral siloxanes such as 1,3,5,7 tetramethylcyclotetrasiloxane (D_4), Octakis(dimethylsiloxy)-T_8-Silsequixane (POSS) and heptamethyl cyclotetrasiloxane (D_3D) are a class of important inorganic-organic hybrid compounds, which have often been used to improve the properties of the materials.[2]



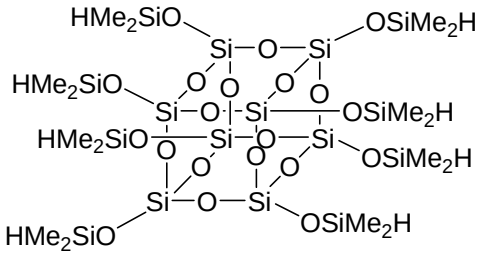
D_3DH



PDMS



D_4H



T_8H

Figure 1. Structures of linear and cyclic and polyhedral oligosiloxanes.

The self-assembly of the hybrid polymers functionalized with these nanoscale molecules into nanostructures also serve as promising strategy for bottom-up material designs.[3] Many polymeric hybrid materials containing POSS molecules have been found to self-assemble into various interesting nanostructures. For example, polyethylene oxide

tethered with POSS nanocubes self-assemble in aqueous media to form micelles and vesicles. The POSS molecules functionalized with polyoxazoline have been reported to form miceller aggregate in aqueous solvent. Cardeon and Coughlin synthesized POSS-polystyrenes hybrid, which self-assembles into lamellar or cylindrical morphology in organic solvent. Morphology of D_4-divinylbenzene nanocomposites has also been studied in recent years. Moreover, the incorporation of cyclic/polyhedral siloxanes into hybrid materials, abruptly enhances the materials properties, including increased thermal stability, higher glass-transition temperature, better flame and heat resistance, and enhancements in the modulus and melt strength.[3] These materials have found potential application in ion-conduction[4], nonlinear optics,[5] heterogeneous catalysis[6], solid-phase extraction[7], membranes[8], liquid crystals[9] etc. These enhancements have been reported to apply to a wide range of polymers including polymethacrylates[10], polystyrenics[11], polynorbornenes[12], polyethylene[13], polyepoxide,[14] etc. Therefore, many nanocomposites can be designed on the basis of using such oligosiloxanes with traditional polymers.

The unsaturated polymers such as polyisoprenes and polybutadienes represent an ideal class of polymers for polymer tailoring reactions since these polymers contain active double bond per each monomer unit after polymerization. Among them the polybutadienes are well known, least expensive and are readily available with a wide range of molecular weights with different degree of unsaturation. Moreover, their unique elastomeric properties make these polymers indispensable for the production of synthetic rubber. Various catalytic and non-catalytic reactions across the double bonds are known which can be performed to achieve new organo-functional polymers. The most common catalytic methods to modify these polymeric double bonds can be classified as

hydrogenation,[15,16] hydroformylation,[15,17] hydrocarboxylation,[15,18] epoxidation,[15,19] oxidation,[20] hydrosilylation[15,21,22] and vinyl coupling reactions.[23] In addition, a considerable number of patents have been granted on different ways of functionalization of polybutadienes.[15] Although a large number of functional materials have been generated based on various catalytic reactions on these polymers, very little is known about these polymers covalently linked with cyclic/polyhedral oligosiloxanes.

Our group has recently reported a highly selective and mild synthetic route to silyl-functionalization of 1,2-polybutadienes (PBD) via Pt-nanocluster-catalyzed hydrosilylation of olefin bonds.[24] Unlike other catalytic systems, our system was found to be equally effective with all varieties of functional silanes such as halo-, alkyl-, aryl- and alkoxy- silanes affording high yields and selectivities. In addition, all the hydrosilylation reactions were found to be very clean with the ease of product separation and purifications. As a continuation of our efforts towards polymer modifications, our objective is to design and synthesize the hybrid polymers based on various linear, cyclic and polyhedral siloxanes. In this chapter, we describe the strategy to generate families of new inorganic/organic hybrid polymers derived from hydrosilylation of polybutadienes with various well-defined oligosiloxanes. In addition, the thermal and morphological behaviors of such new materials are also described.

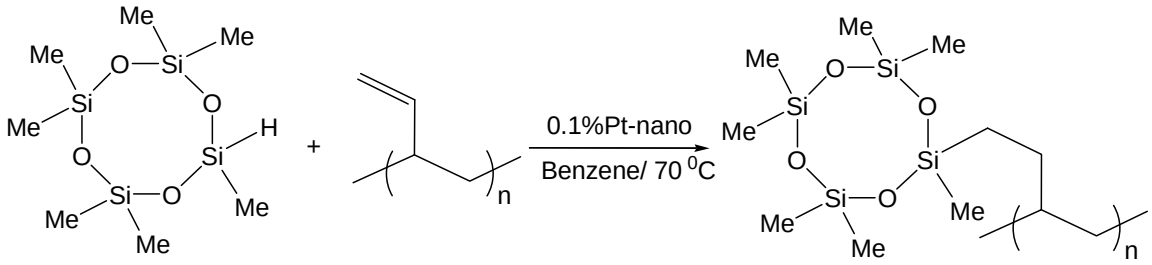
5.1. Synthesis of Siloxy-Functionalized Polybutadiene

The synthesis of siloxy-functionalized polybutadienes has been achieved via catalytic hydrosilylation of pendant olefin bonds of polybutadiene with available Si-H groups of siloxane molecule. Pt-nanoclusters have been used as a catalyst, due to their high efficiency as hydrosilylation catalyst in terms of selectivity as well as recyclability.

Four structurally different oligomeric siloxanes (PDMS, D_3DH, D_4H and T_8H, Figure 1) have been employed for our studies.

To investigate the catalytic efficiency and selectivity of Pt-nanoclusters in hydrosilylation reaction of PBD with oligosiloxanes, the reaction of (D_3DH) with PBD was studied in presence of Pt-nanoclusters (Scheme 1). In a typical procedure, a Schlenk tube (10 mL), equipped with magnetic stirrer and oil bath was charged with Pt-nanoclusters (0.005 g, 0.001 mmol), degassed and flushed with nitrogen. The PBD (0.056 g, 1.0 mmol) dissolved in dry benzene (2 mL) was added to the schlenk followed by the addition of D_3DH (1.0 mmol) under the constant flow of nitrogen. After a few minutes of stirring, the reaction mixture turned into light brown homogeneous solution, indicating the formation of soluble nanoclusters. The reaction was monitored by ^1H NMR spectroscopy. After the completion of reaction, the catalyst was separated by centrifugation (1 h) and the solvent was evaporated to obtain the product polymer **I** (1.0 mmol) as a pale yellow viscous liquid. The product thus obtained was analyzed by GPC and ^1H, ^{13}C, DEPT, ^{29}Si NMR spectroscopic techniques.

Scheme 1. Hydrosilylation of 1, 2-polybutadiene (PBD) with D_3DH via Pt-nanocluster Catalysis.



D_3DH (1 equiv) Polymer **I**

Gel permeation chromatography (GPC) was used to determine the molecular weight and chain length properties of functionalized polymers with reference to polystyrene standards. The GPC chromatograms of the products have clearly been shifted toward the high molecular weight region, while retaining a narrow molecular weight distribution (*M*w/*M*n = 1.4-1.5). This analysis confirmed that no other side reactions such as chain scission, cross-linking, etc. occurred during the course of the hydrosilylation reaction, leaving the large-scale molecular structure intact (Figure 2).

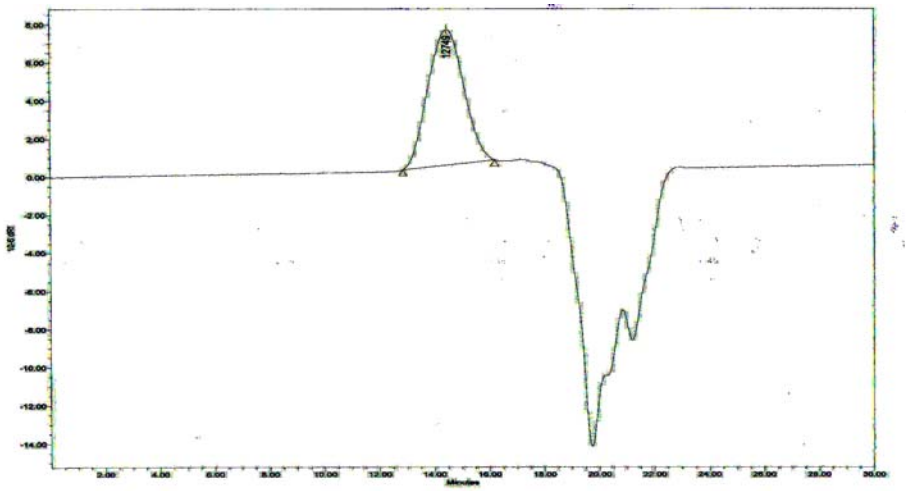


Figure 2. GPC chromatogram of polymer **I**.

^{1}H, ^{13}C and ^{29}Si NMR studies of the products suggested that the hydrosilylation of PBD occurs selectively via an anti-Markovnikov addition, i.e., the Si-atom being attached at the terminal position of olefin bonds (*β*-product) (Figure 3-5).

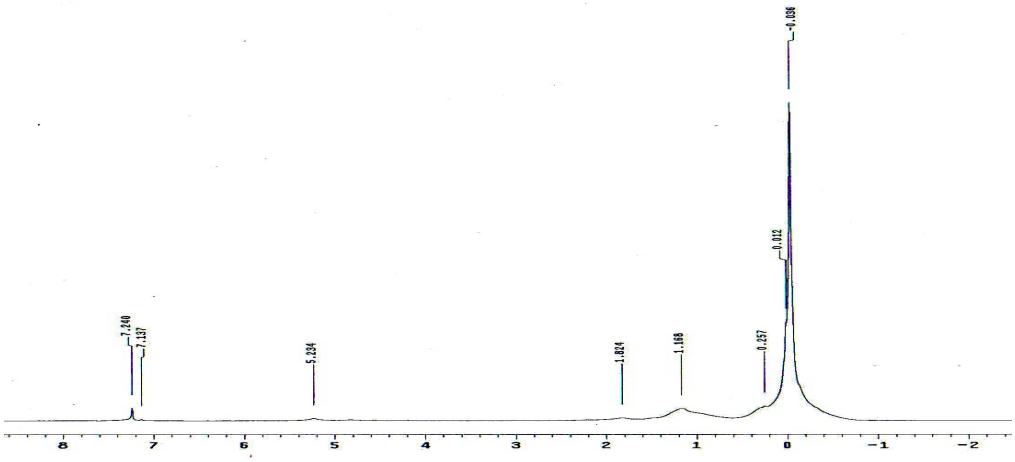


Figure 3. ^{1}H NMR of D_3DH and polymer **I**.

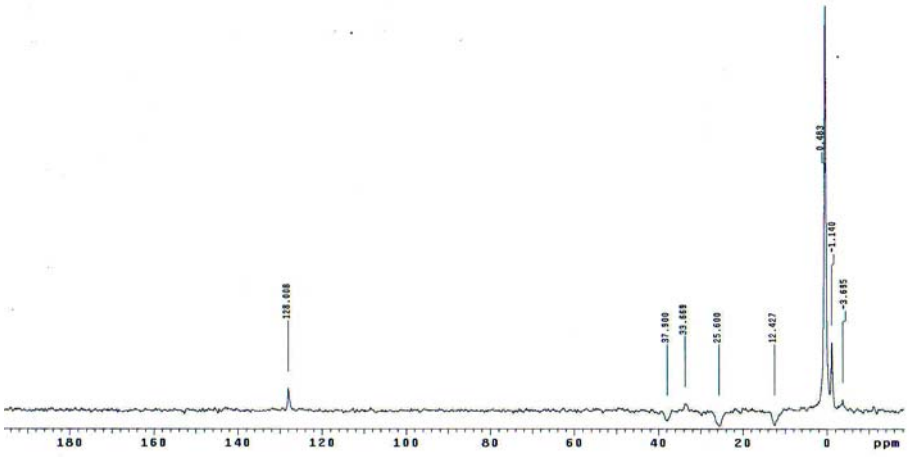


Figure 4. ^{13}C NMR of D_3DH and polymer **I**.

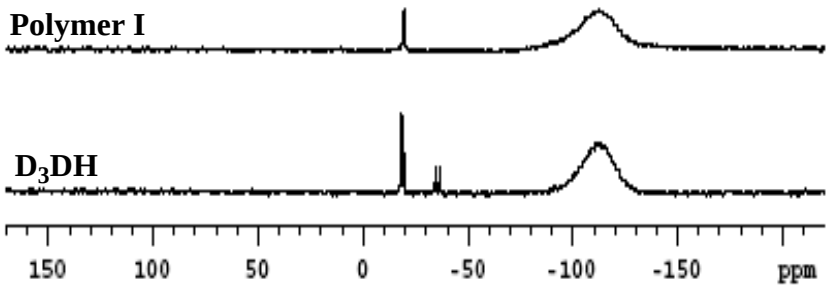


Figure 5. ^{29}Si NMR of D_3DH and polymer **I**.

The hydrosilylation of PBD was also achieved under identical reaction conditions using other siloxanes such as PDMS (1.0 equiv. Si-H), D_4H (2.0 equiv. Si-H) and T_8H (4.0 equiv of Si-H) respectively (Scheme 1). All the polymer products are characterized by GPC and ^{1}H, ^{13}C, DEPT, ^{29}Si NMR spectroscopic techniques. The GPC results are summarized in Table 1.

Table 1. Hydrosilylation of PBD with various oligosiloxanes.

Oligosiloxane (Eqv.)	[Olefin]/ [Si-H]	Polymer	Calculated[a] Mol.Wt.(Mn)	Experimental Mol. Wt.(Mn)	PDI
D_3DH (1.0 eqv)	1:1	**I**	13440	11300	1.7
PDMS (0.5 eqv)	1:1	**II**	27480	13900	2.2
D_4H (0.5 eqv.)	1:2	**III**	14000	13600	2.0
T_8H (0.25 eqv.)	1:4	**IV**	49280	39500	2.5

[a]Calculated molecular weight are based on their idealized structures as shown in Figure 9.

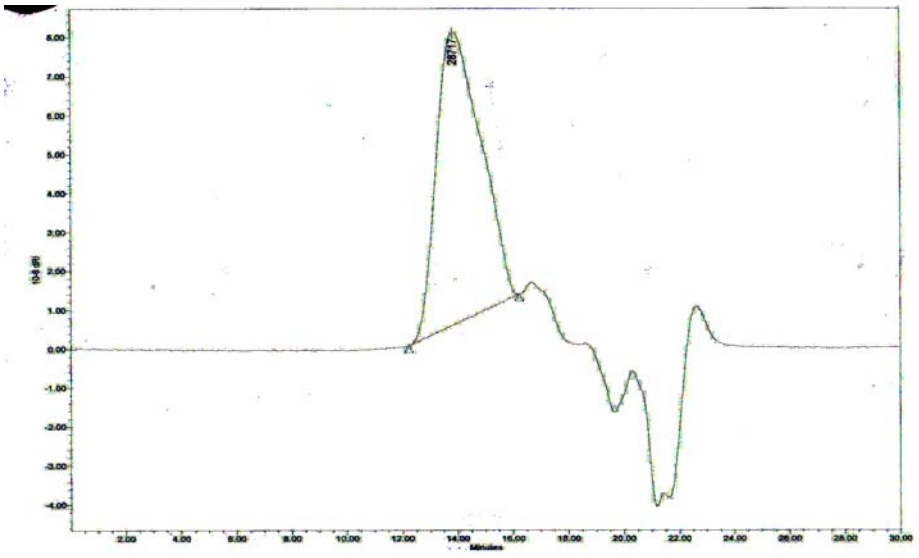


Figure 6. GPC Chromatogram of Polymer **II**

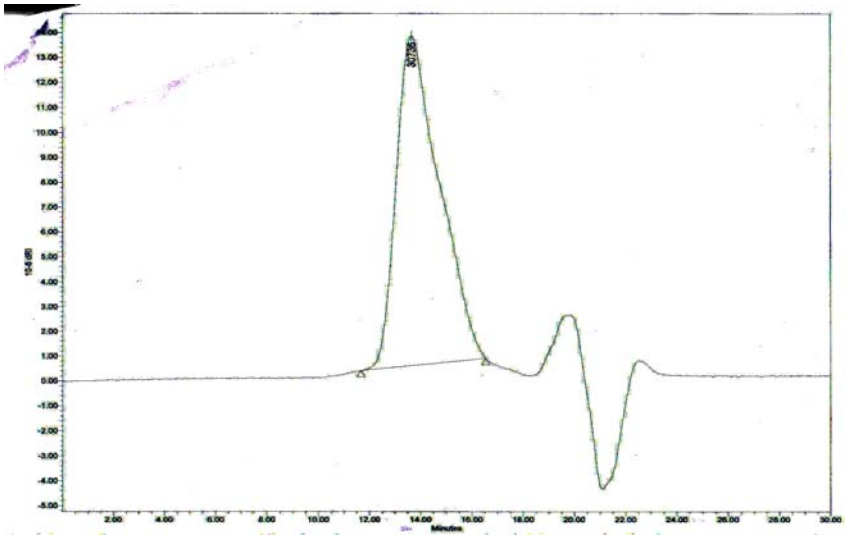


Figure 7. GPC Chromatogram of Polymer **III**

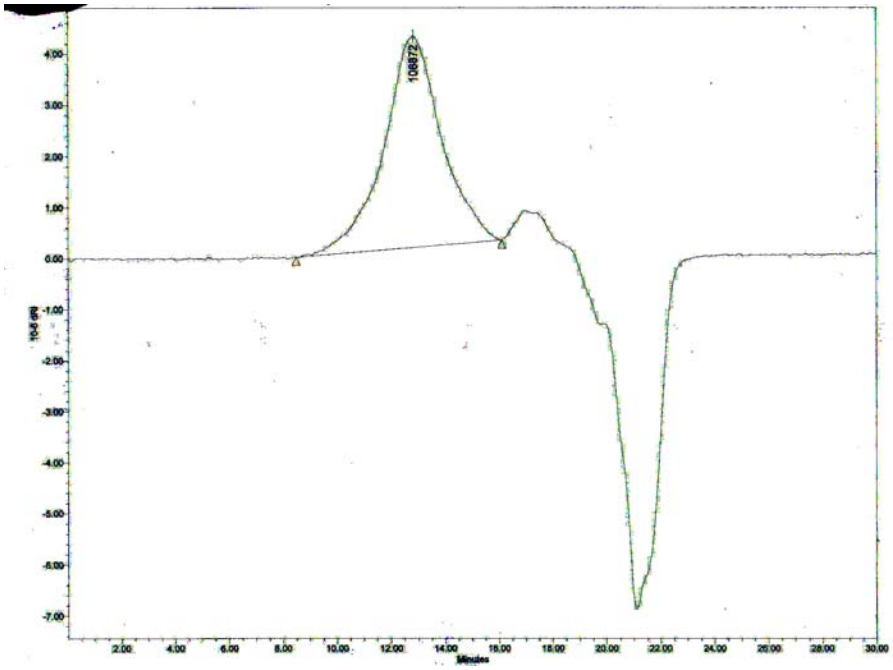


Figure 8. GPC Chromatogram of Polymer **IV**

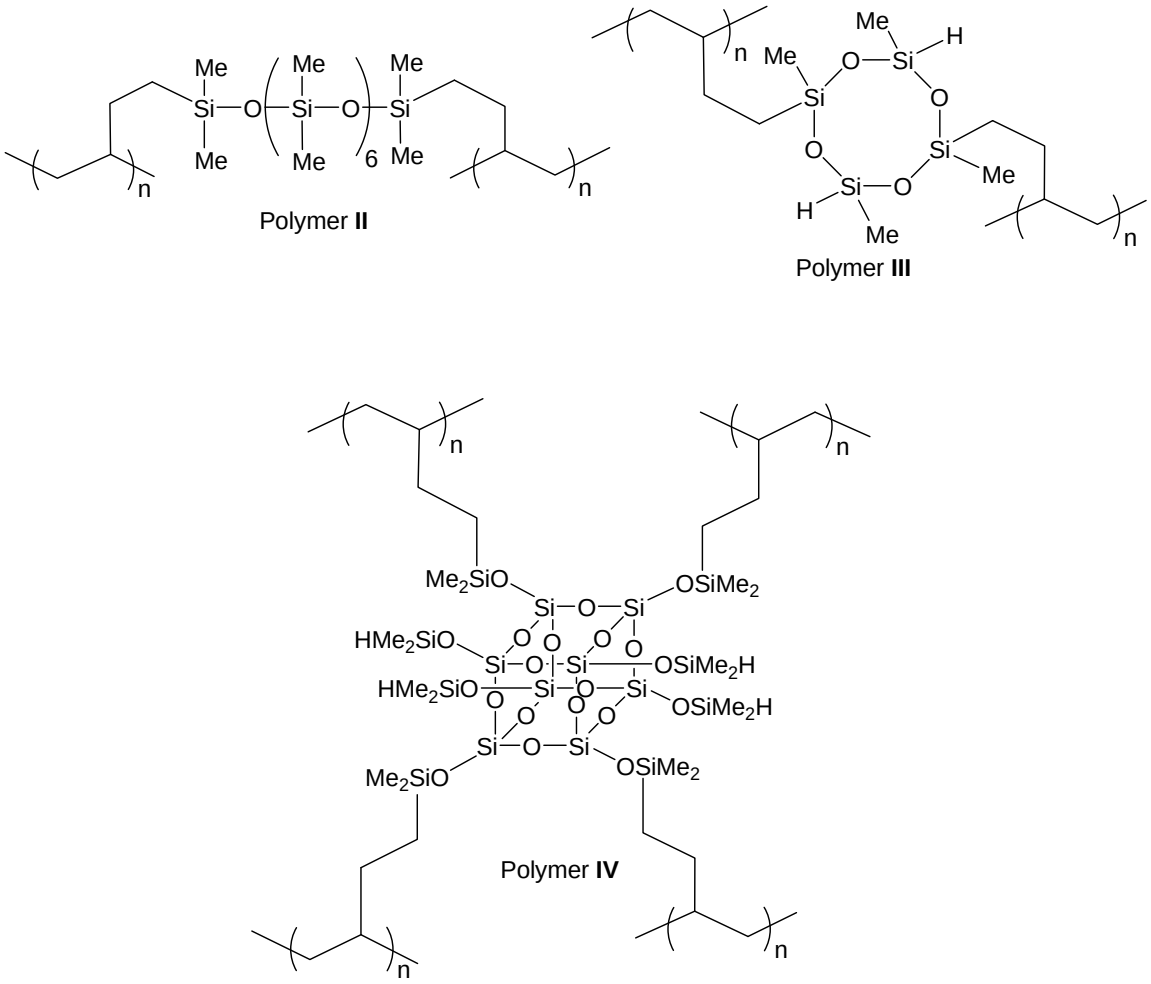
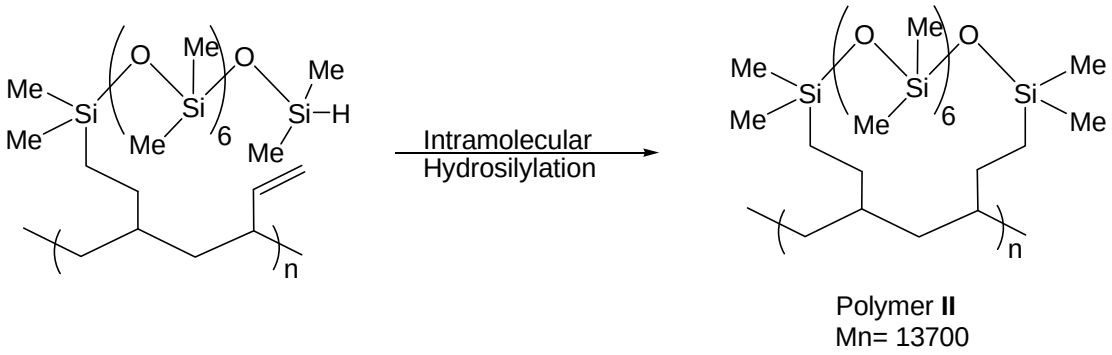


Figure 9. Idealized structures of the polymer **II**, **III** and **IV**.

The structure and chain-length properties of the polymers were studied by ^{1}H, ^{13}C, DEPT, ^{29}Si NMR and GPC techniques. ^{1}H NMR and ^{13}C NMR showed complete hydrosilylation of olefin bonds, without any side reactions involving remaining Si-H bond (Figure 10-14). The number average molecular weight (Mn) obtained for polymer **I**, **III** and **IV** were in good agreement with those calculated from their microstructure as shown in Figure 1. In case of polymer **II**, the molecular weight obtained from GPC analysis, was much lower than that calculated from its idealized structure. One possible

reason for this deviation could be the formation of ring structure via intramolecular hydrosilylation (Scheme 2).

Scheme 2. Possible mechanism of formation of ring structure via intramolecular hydrosilylation reaction



Polymer **II**
Mn= 13700

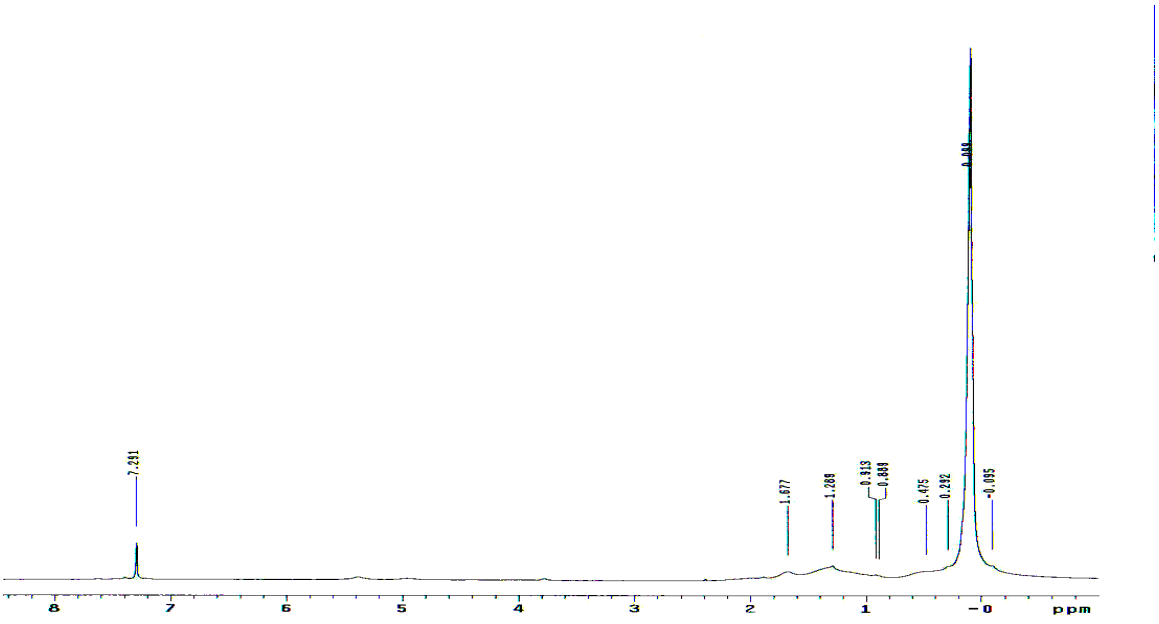


Figure 10. ^{1}H NMR Spectra of Polymer **II**

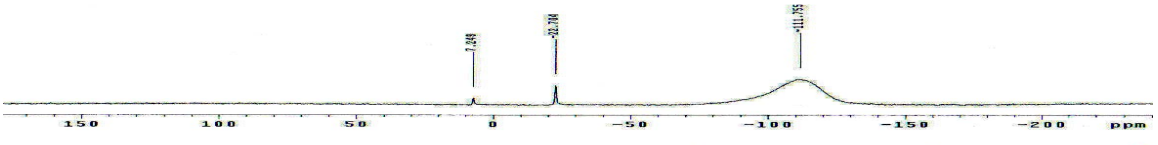


Figure 11. ^{29}Si NMR Spectra of Polymer **II.**

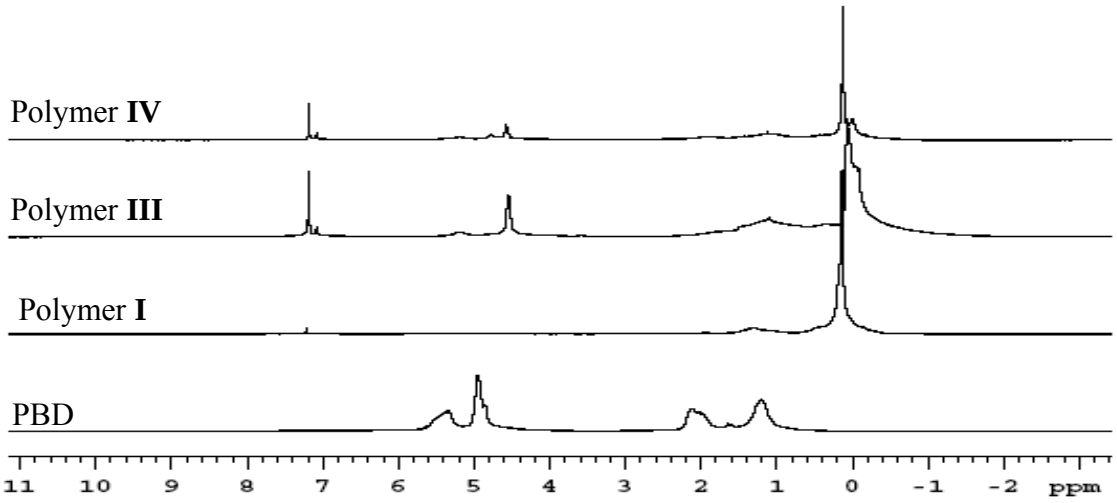


Figure 12. ^{1}H NMR Spectra of Polymer **I, II, III**

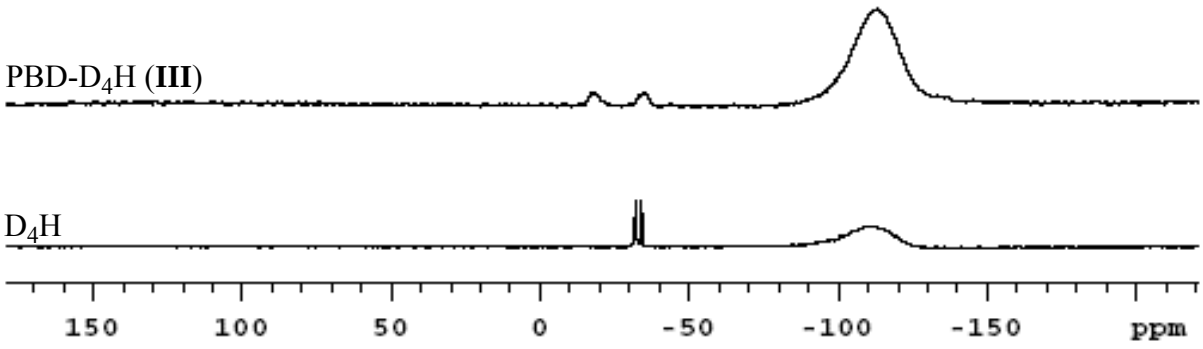


Figure 13. ^{29}Si NMR Spectra of D_4H and polymer **II**

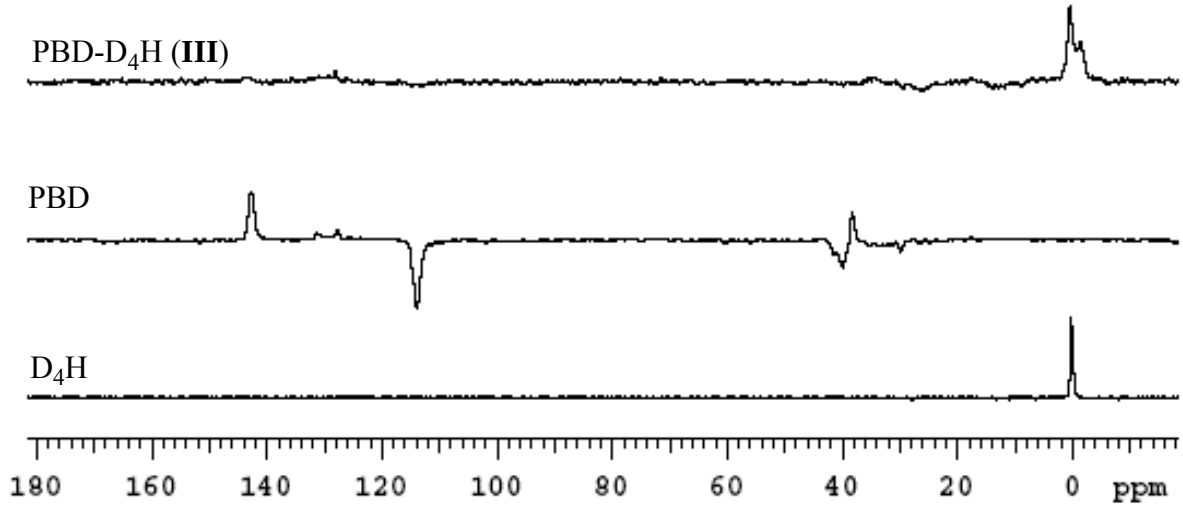


Figure 14. ^{13}C NMR Spectra of PBD, D_4H and polymer **III**

5.2. Thermal Analysis of Siloxy-Functional Polybutadiene

The thermal stability of polymers I, II, III and IV were evaluated by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

The thermogravimetric analysis (TGA) of polymer **I** revealed that the initial decomposition of the polymer started at 200 ^{o}C with around 5 % weight loss, which was probably due to the unreacted monomer (D_3D) occluded in the polymeric network. Around 350 ^{o}C the main degradation initiated and complete decomposition of the

polymer was observed at around 450 ^{o}C (Figure 15). The main degradation stage is due to decomposition of $SiCH_3$, $SiCH_2$, C-C bond etc. The DSC thermogram (Figure 16) indicated the glass transition temperature of –65 ^{o}C. The TGA of polymer **II**, has also shown a similar thermogram, with an initial weight loss started at around 350 ^{o}C (Figure 17). The DSC thermogram (Figure 18) of polymer **II** indicated the glass transition temperature of –17 ^{o}C (Tg for 1,2 polybutadiene is –25 ^{o}C). The excellent thermal stability of polymer **III** and **IV** was demonstrated by TGA experiments in which heating upto 800 ^{o}C at a rate of 10 ^{o}C/min in nitrogen resulted in weight loss of ~ 25 % and ~ 15% (Figure 19 and 20) respectively. In the DSC thermogram of **III** and **IV**, an exothermic peak at 120-160 ^{o}C was observed (Figure 21 and 22), which can be attributed, to the thermal induced radical reaction of free vinyl groups.[25]

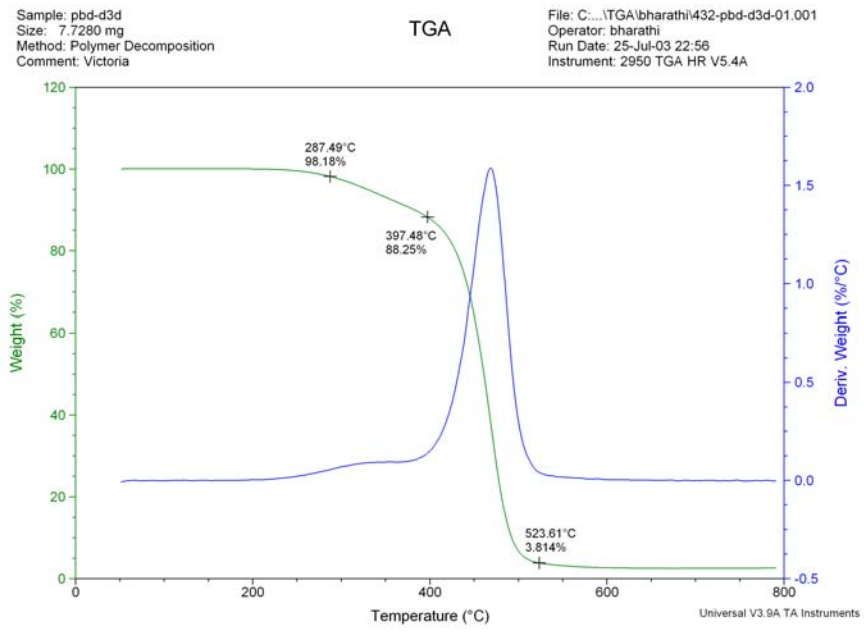


Figure 15. TGA of polymer **I**

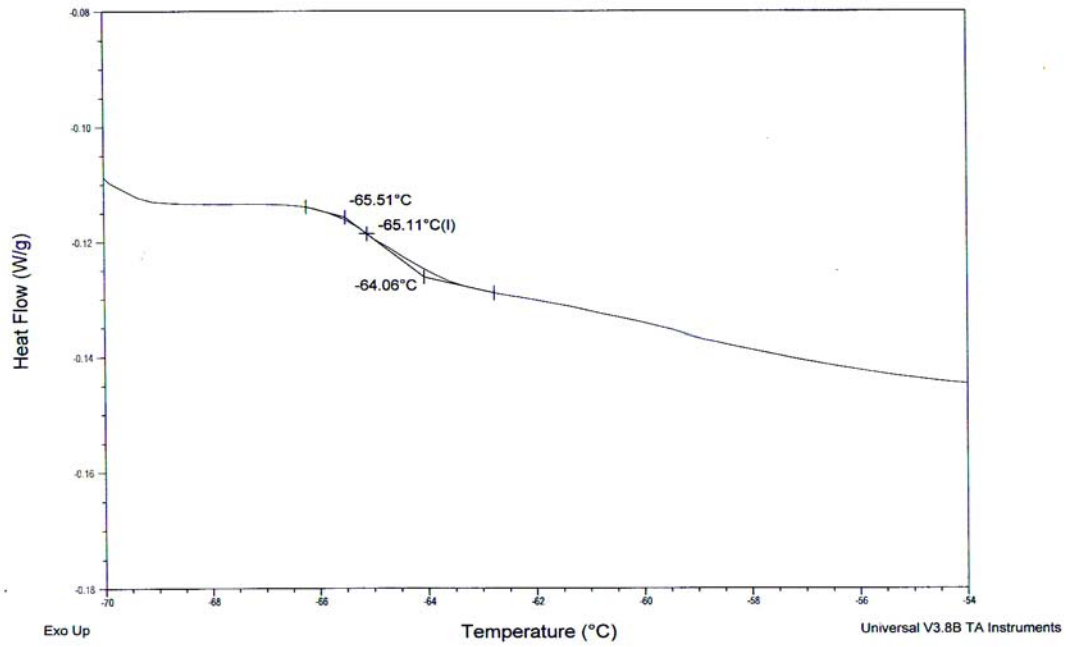


Figure 16. DSC of polymer **I**

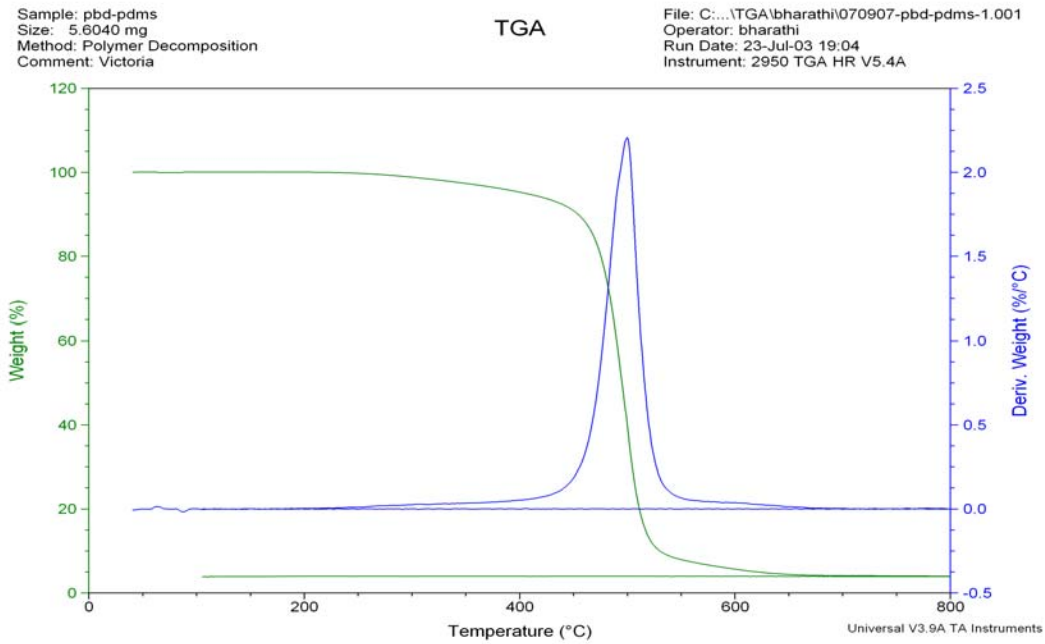


Figure 17. TGA of Polymer **II**

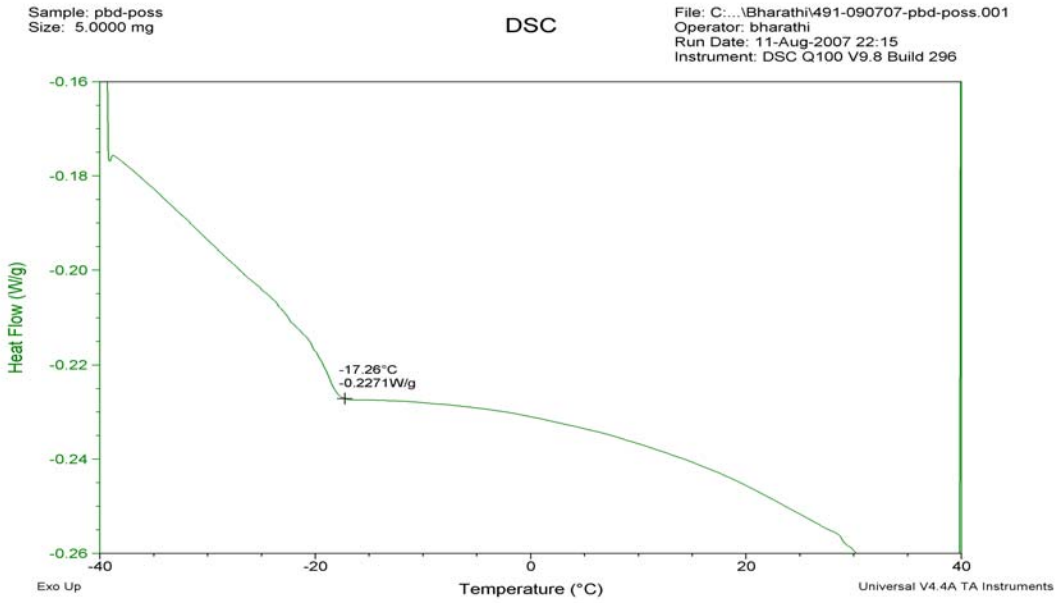


Figure 18. DSC of Polymer **II**

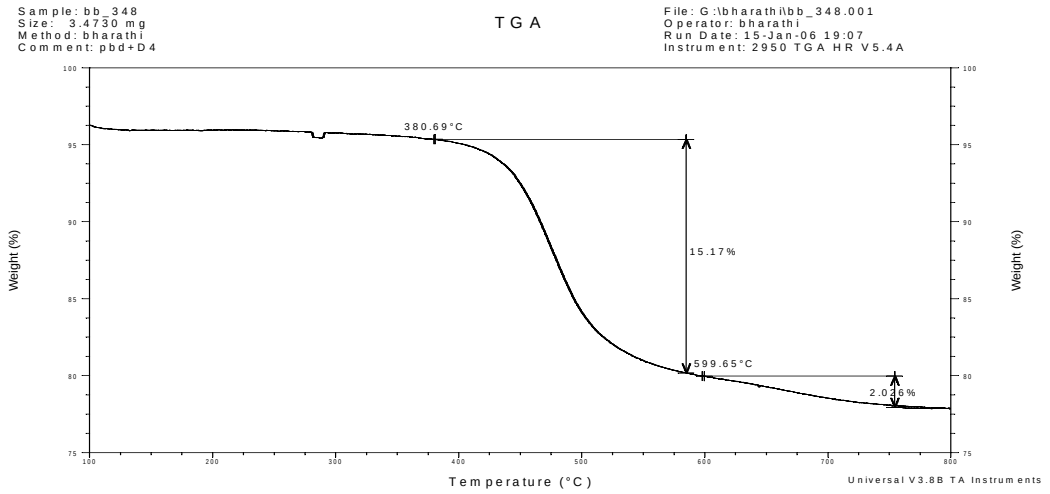


Figure 19. TGA of Polymer **III**

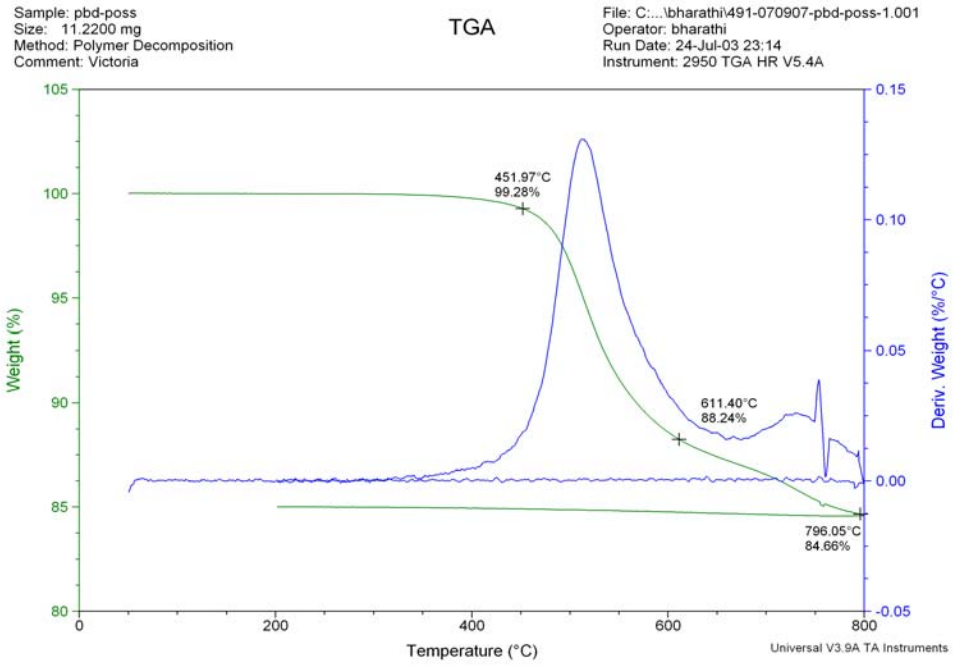


Figure 20. TGA of polymer **IV**

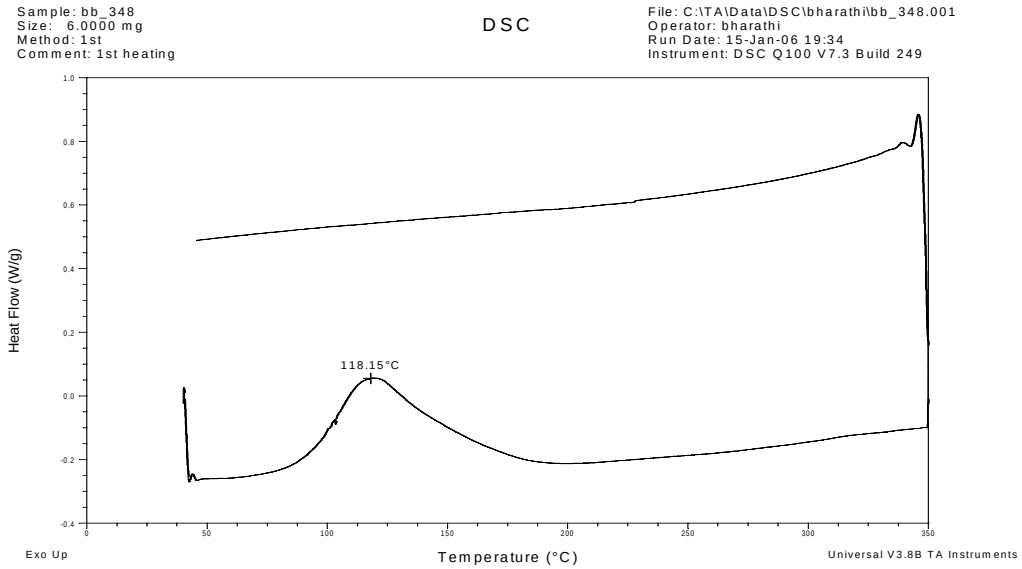


Figure 21. DSC of polymer **III**

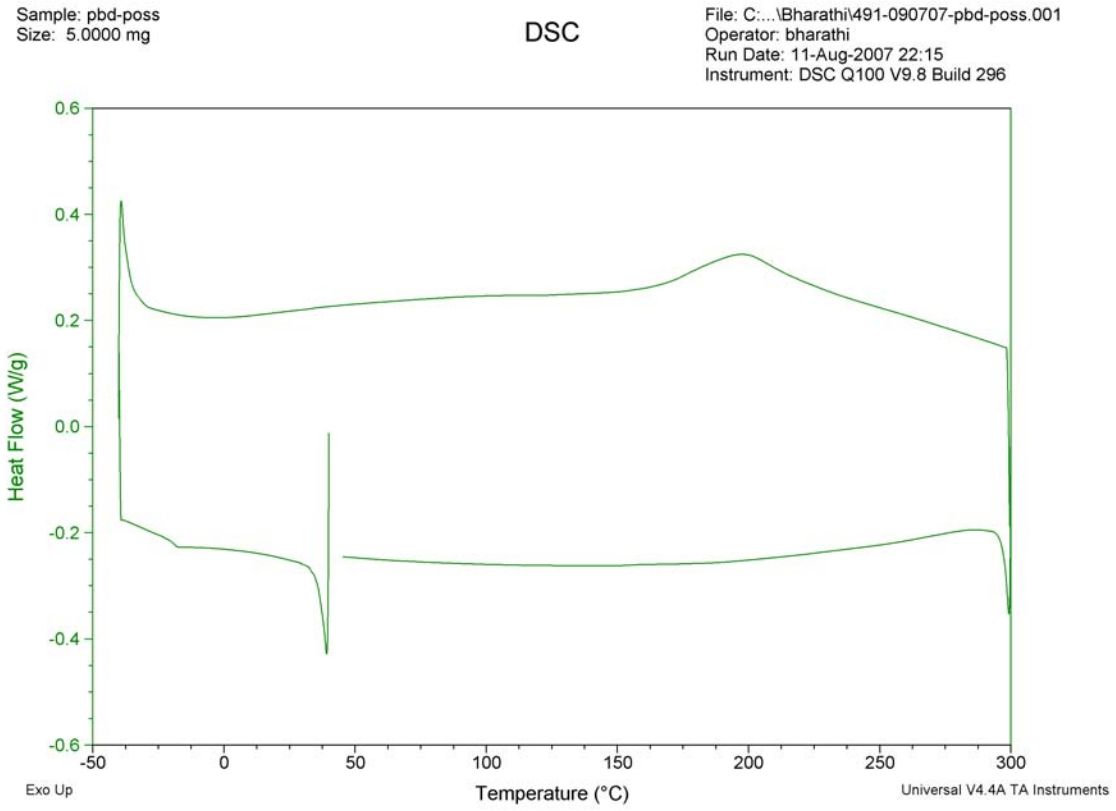


Figure 22. DSC of Polymer **IV**

5.3. Morphological Analysis

Morphologies of polymers **I, II, III, IV** were characterized by AFM, SEM, TEM techniques. In order to study the morphology of the polymers **I-IV**, the samples were dissolved in THF (0.005 mg/mL) and deposited on a mica surface by means of spin coating. After drying for 24 h at room temperature, the hybrid thin films obtained were studied by AFM and SEM. The AFM analysis of polymer **I,** revealed the presence of vesicular morphology with an average diameter of 100-150 nm (Figure 23). The SEM analysis of the film on a larger area has also shown self-assembly of similar vesicular structures with the diameter in the range of 100 nm (Figure 24). The AFM images of polymer **II** and **III**, as shown in Figure 25 and 27 respectively, has revealed a uniform

cross-linked tubular network. This morphology was also observed in TEM and SEM images of polymers **II** and **III** (Figure 26, 28 and 29). The AFM and TEM studies of polymer **IV** have shown the self-assembly of the polymer into nano-rings (donut shape) with an inner and outer diameter of 30 nm and 60 nm respectively (Figure 30 and 31). Thus the results of AFM, TEM and SEM substantiate that the nanocomposites were successfully obtained in all cases of polymer **I- IV**.

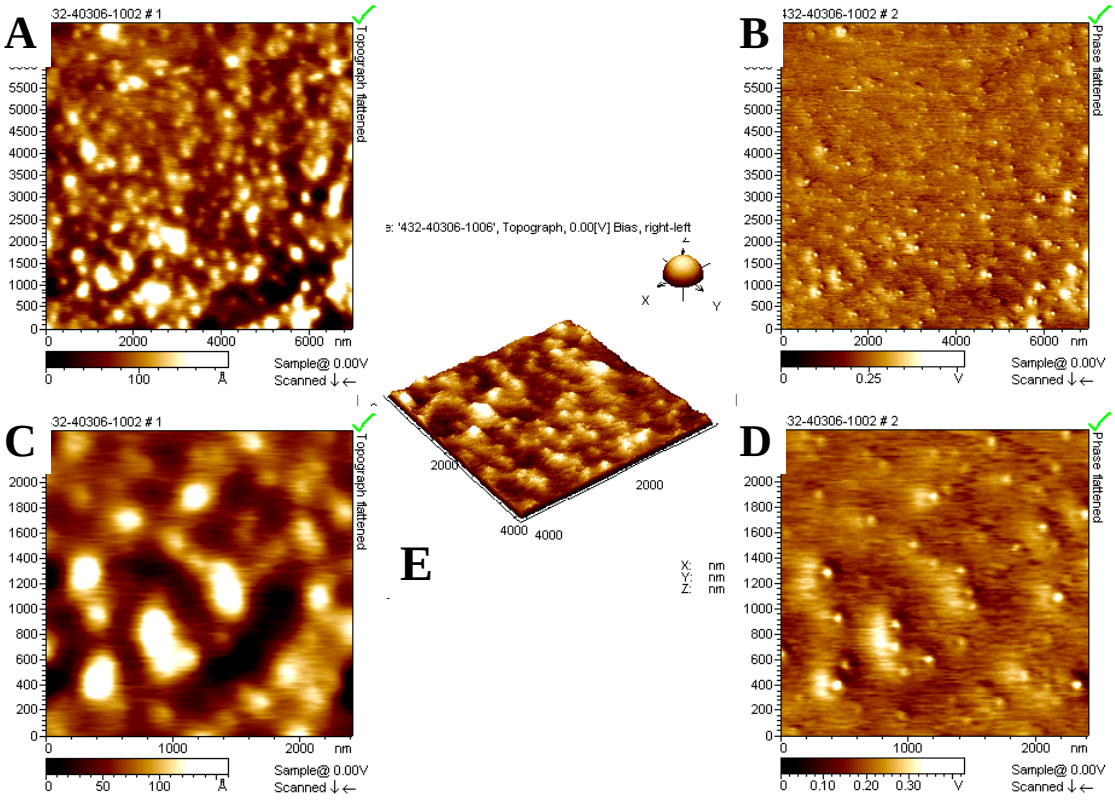


Figure 23. AFM analysis of polymer **I** (A) topography lower magnification and (B) corresponding phase image (C) topography higher magnification and (D) corresponding phase image. (E) 3D image.

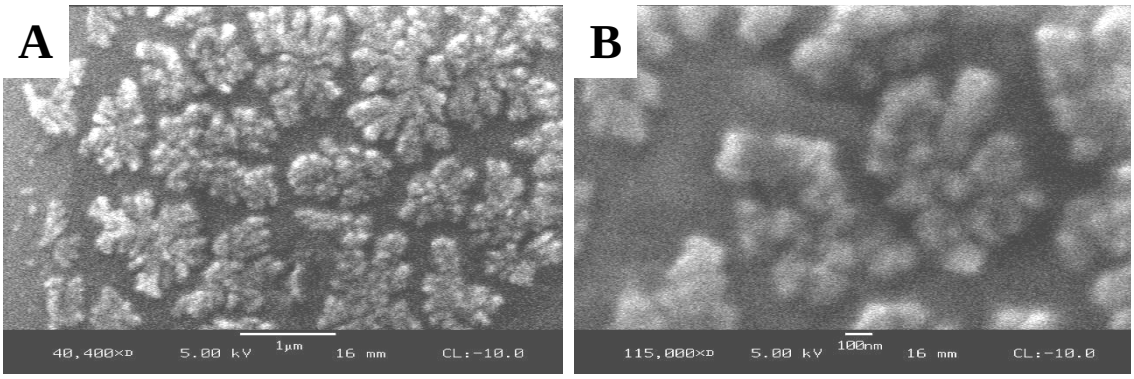


Figure 24. SEM analysis of polymer **I** (A) lower magnification (B) higher magnification.

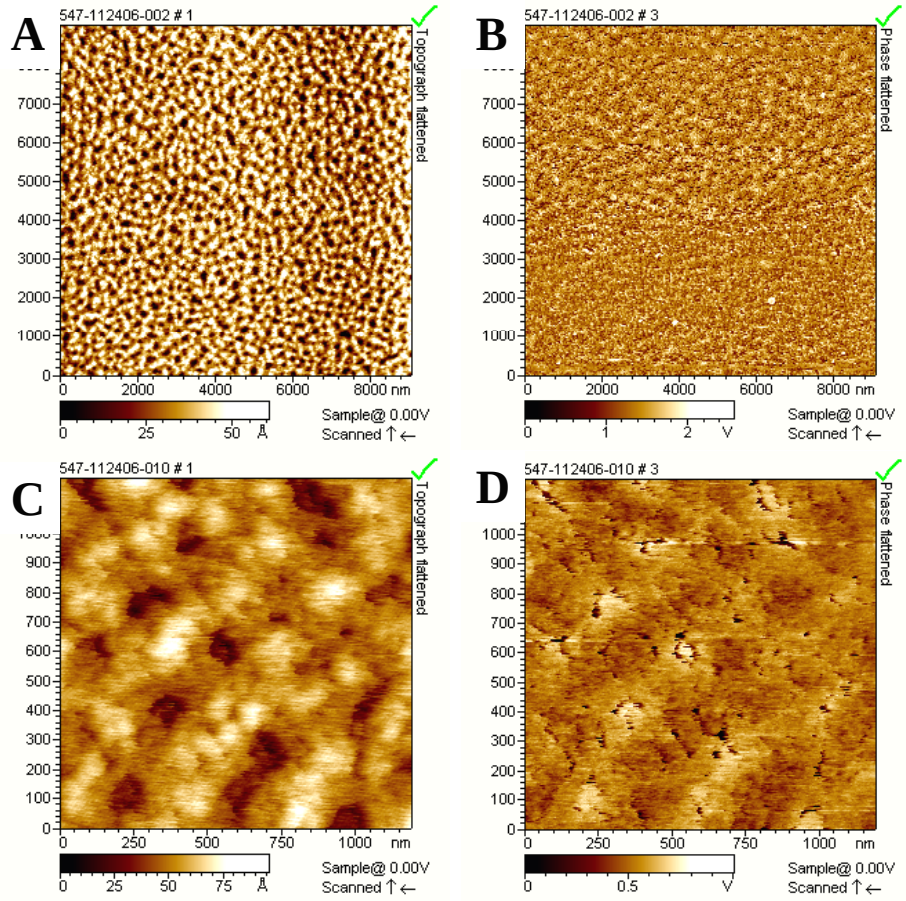


Figure 25. AFM analysis of polymer **II** (A) topography lower magnification and (B) corresponding phase image (C) topography higher magnification and (D) corresponding phase image.

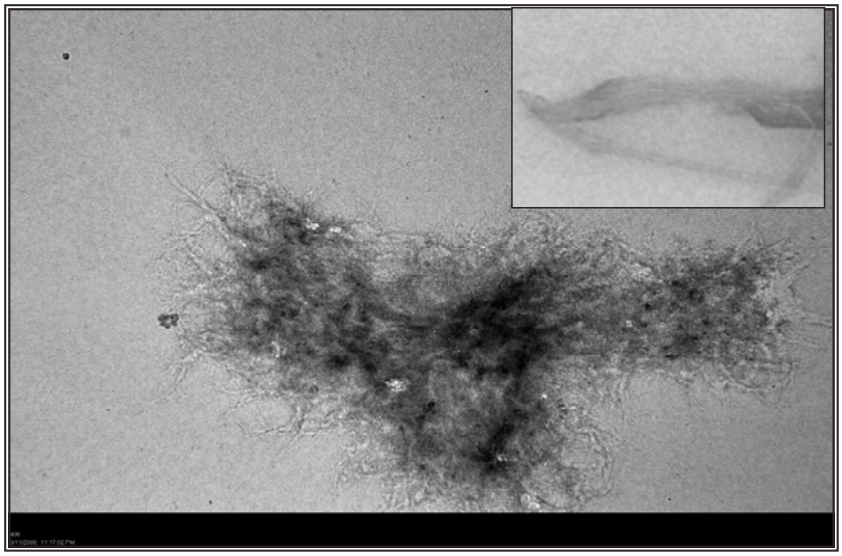


Figure **26**. TEM Image of polymer **II** (inset higher magnification)

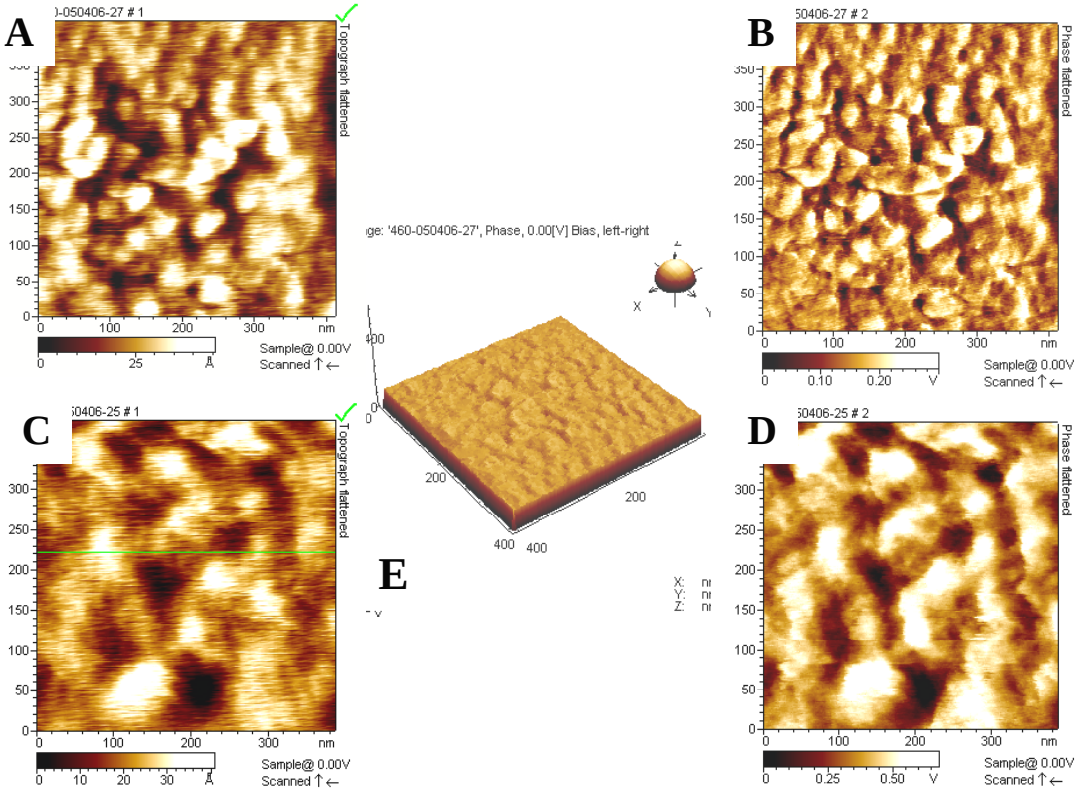


Figure 27. AFM analysis of polymer **III** (A) topography lower magnification and (B) corresponding phase image (C) topography higher magnification and (D) corresponding phase image.

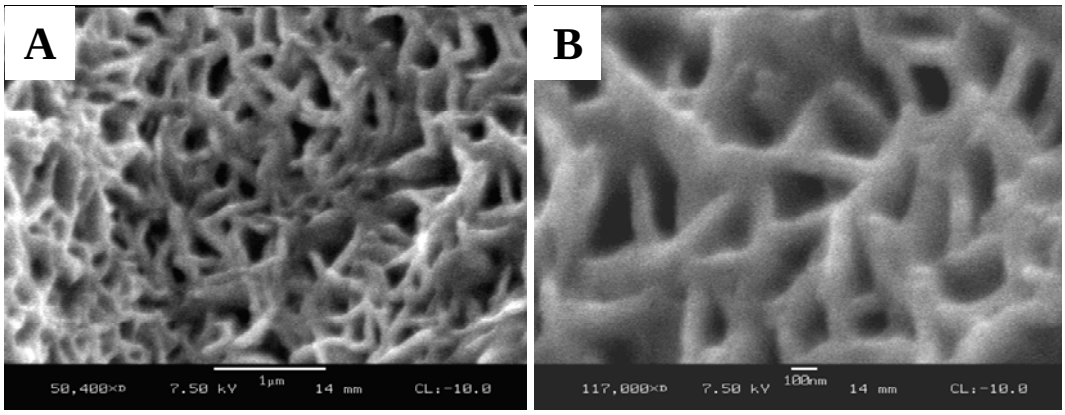


Figure 28. SEM analysis of polymer **III** (A) Lower magnification (B) Higher magnification.

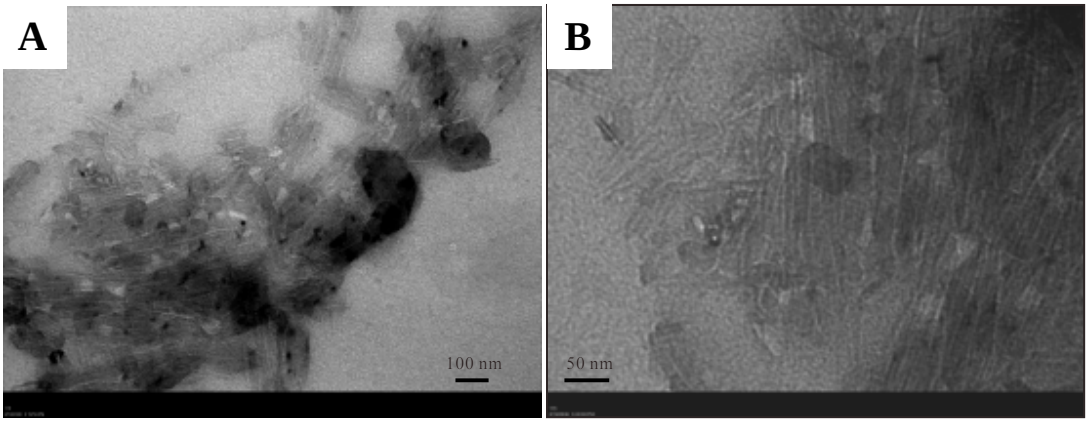


Figure 29. TEM Image of polymer **III** (A) Lower magnification (B) higher magnification.

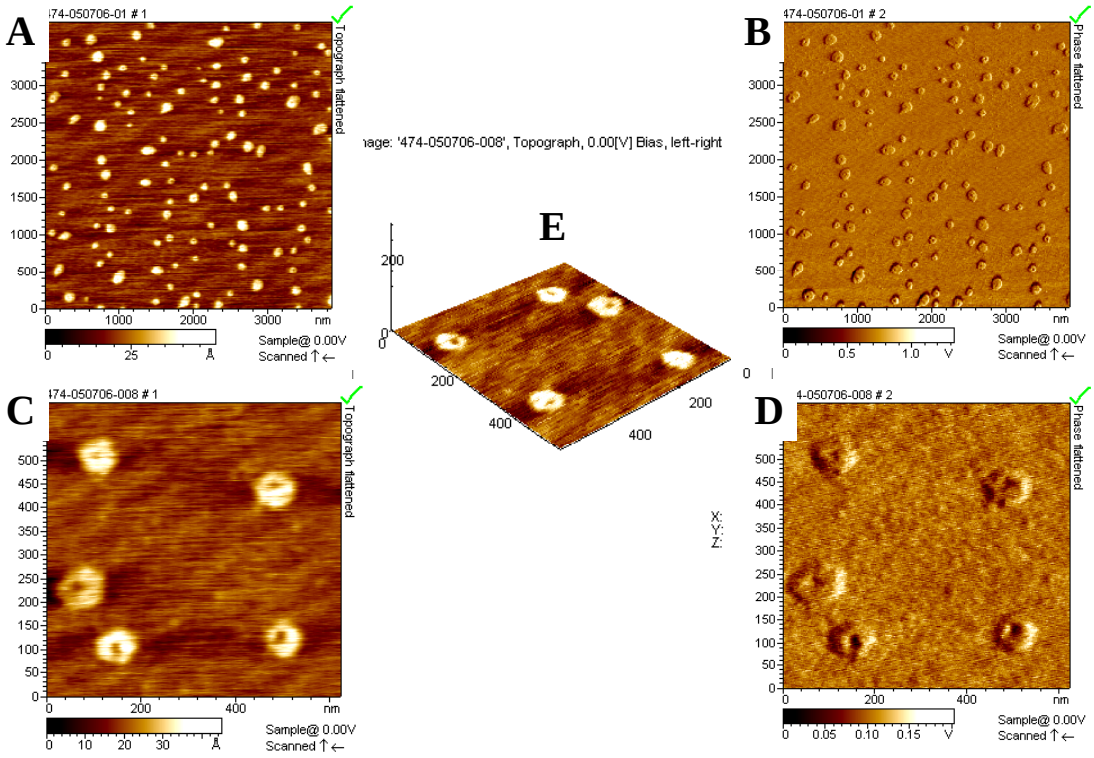


Figure 30. AFM analysis of polymer **IV** (A) topography lower magnification and (B) corresponding phase image (C) topography higher magnification and (D) corresponding phase image.

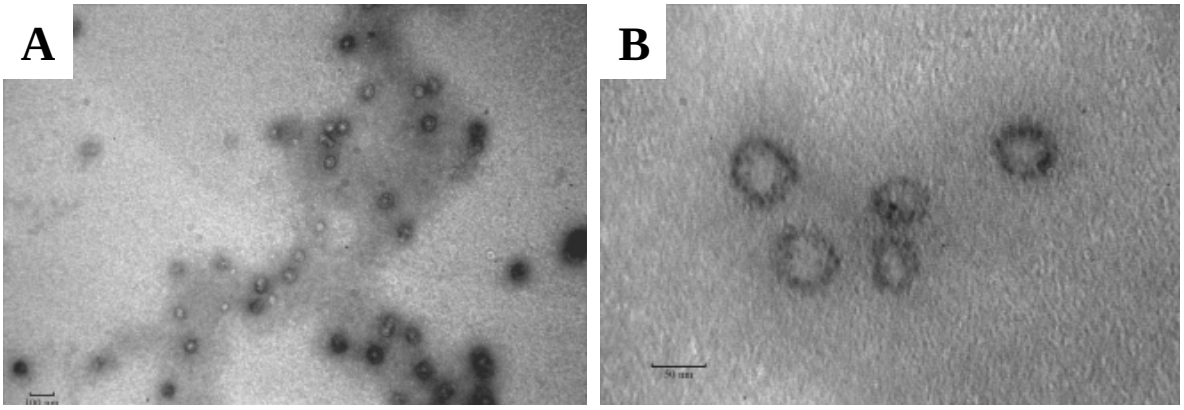


Figure 31. TEM image of polymer **IV** (A) lower magnification (B) higher magnification.

5.4. Conclusion

Self-assembled I/O hybrid polymer nano-structures have been obtained from polybutadienes hydrosilylated with cyclic-siloxanes such as heptamethyl cyclotetrasiloxane (D_3D), 1,3,5,7 tetramethylcyclotetrasiloxane (D_4), octakis(dimethyl Siloxy)-T_8-Silsequixane (T_8) and linear siloxanes of polydimethylsiloxane (PDMS) using Pt-nanocluster catalysis. The nano-composites obtained from siloxy functional polybutadienes are found to be in the range 50-100 nm. This route provides a one-step template, free access to hybrid nano-structures in good yields. The morphological studies by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) have been presented in this chapter.

5.5. Experimental Section

General Information. All of the experiments and manipulations were performed under dry oxygen-free nitrogen using standard Schlenk-line techniques. All the Solvents were purchased from EM science (Merck) and distilled over sodium/benzophenone before use. PMHS (Mw ≈ 2000), $Me_2Pt(COD)$, 1,2-polybutadienes (Mn=2180) and silanes were purchased from Aldrich Chemical Co., and Gelest Chemical Co. and used without further purification. ^1H NMR, ^{13}C NMR and ^{29}Si NMR spectra were recorded on 200 MHz and 600 MHz Varian Unity NMR instruments with $CDCl_3$ as an internal standard. GPC analysis was carried out on Alliance GPCV 200 (Water) instrument, equipped with two silica columns, HRSE and HR-1 with the pore size range of 100-5000 Å and 2000-4x10^6 Å respectively. This instrument was calibrated using polystyrene standards. THF was used as an eluent at the flow rate of 1mL/min at 40 ^0C. A third order calibration curve was used to measure the molecular weight of unknown samples**.** Philips CM 100

transmission electron microscope (TEM) was employed to examine the reaction mixture for the presence of Pt-nanoclusters. Scanning electron microscope Amray 1910 (SEM) was used to analyze solid Pt-nanocluster. Thermogravimetric analysis (TGA) of functional polymers was carried out in a TGA 2950 thermogravimetric analyzer, TA instruments, in the range of 25-800 ºC at scanning rate of 10ºC /min, under nitrogen flow. Differential scanning calorimetry, DSC, was performed using TA instruments, DSCQ100 model. Samples were run in the temperature range between –80 ^{o}C to 200 ^{o}C under nitrogen flow, at a scanning rate of 10ºC/min. The surface morphology was recorded using 'Picoscan' tapping mode AFM system (Molecular Imaging, USA). The force constant of the cantilever was 40 N/m. All images were recorded under an atmosphere of air at room temperature.

Typical Procedure for the Synthesis of Siloxy Functional Polybutadiene.

In a typical procedure, a schlenk tube (10 mL), equipped with magnetic stirrer and oil bath was charged with Pt-nanoclusters (0.01 g, 0.001 mmol Pt), degassed and flushed with dry nitrogen. The PBD (0.104 g, 2 mmol) dissolved in dry benzene (2 mL) was added to the Schlenk followed by the addition of Silane (2.4 mmol) under the constant flow of nitrogen. After few minutes of stirring, the reaction mixture turned into light brown homogeneous solution, indicating the formation of soluble nanoclusters. The reaction progress was monitored by ^{1}H NMR spectroscopy. On completion of the reaction, the catalyst was separated by centrifugation (1 h) and the solvent was evaporated into round-bottom flask when polymer product (0.29 g, 2.0 mmol), was obtained as light yellow viscous liquid.

Multinuclear NMR data of the product(s).

Polymer **I**

^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) –0.036 (s, 21H), 0.5-1.9 (br, 7H);

^{13}CNMR/DEPT ($CDCl_3$, 200 MHz): δ (ppm) –4.83 (-Si*CH_3*), 12.42 (-CH_2*CH_2*Si-), 25.6 (-*CH_2*CH_2Si-), 33.66 (-*CH*CH_2-), 37.9 (-CH*CH_2*-);

^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) –20.096 (s)

Polymer **II**

^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) –0.099 (s, 48H), 0.5-1.9 (br, 7H);

^{13}CNMR/DEPT ($CDCl_3$, 200 MHz): δ (ppm) 0.72 (-Si*CH_3*);

^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) –22.70 (s), 7.24 (s)

Polymer **III**

^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) 0.12 (s, 6H), 0.24 (s, 6H), 0.2-2.0 (br, 14H);

^{13}CNMR/DEPT ($CDCl_3$, 200 MHz): δ (ppm) –1.43 (-Si*CH_3*), 0.362 (-Si*CH_3*) 12.42 (-CH_2*CH_2*Si-), 26.32 (-*CH_2*CH_2Si-), 34.58 (-*CH*CH_2-), 38.9 (-CH*CH_2*-);

^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) –17.01(br), -35.23 (br)

Polymer **IV**

^{1}HNMR ($CDCl_3$, 200 MHz): δ (ppm) –0.145 (s, 48H), 0.5-1.9 (br, 7H), 4.61 (s, 4H);

^{13}CNMR/DEPT ($CDCl_3$, 200 MHz): δ (ppm) –0.27 (-Si*CH_3*);

^{29}SiNMR ($CDCl_3$, 600 MHz): δ (ppm) –109.38 (s), –2.1 (d)

5.6. Reference

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CHAPTER 1

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