Silicon Based Polymers

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Editors

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Preface

Interest in silicon-based materials has established an international community whose roots initially dug in organic and silicon chemistry, polymer and sol-gel chemistry, and material science. This fact led Prof. Interrante and Prof. Kawakami to launch a series of workshops that began in Tatsunokuchi, Japan, in 1999 as a satellite workshop to the XIIth International Symposium on Organosilicon Chemistry in Sendai. The first workshop was attended by over 100 participants from Asia, Europe, and the USA and its success emphasized the perceived need for a continuing forum for organosilicon polymer research; a decision was then taken to maintain these workshops on a bi-annual basis. The second and third workshops were held in Canterbury, UK, in 2001, and Troy, USA, in 2003, both workshops achieved a similarly strong international participation.

The fifth meeting was held in France. The city of Montpellier was chosen as organosilicon chemistry plays an important role in the academic field of the University and Ecole de Chimie (The XI International Symposium on Organosilicon Chemistry was organized in Montpellier in 1996, the III Sol-Gel Symposium was organized in Montpellier in 1985 and the XIV edition was also held in September 2007, in the same city). The next ISPO 08 was held in Busan, Korea, 6–8 June 2008, just after the 15th International Symposium on Organosilicon Chemistry.

Those international workshops are designed to highlight advanced research and technological innovations by bringing together scientists with common interests in macromolecular organosilicon compounds and systems. Indeed, silicon-containing materials and polymers are used all over the world in industry, domestic products and high technology applications. Among them, silicones are certainly the most well-known materials, still renewed in their properties and preparation processes and still full of potential. Lesser known (but on the brink of future exploitation) silicon containing-polymers are now close to maturity and some of them are already on the market. Indeed, the chemists have in their grasp polysilsesquioxanes, polycarbosilanes, polysilanes, and polysilazanes, and others that combine silicon and different elements with different linkages. We have learnt how to build chains, dendrimers, hyperbranched and cross-linked networks, physical and chemical gels. The result is a source of materials with applications in materials for optics, electronics, ionic electrolytes, liquid crystals, bio-materials, ceramics and concrete, paintings and coatings etc. all needed to face a myriad of environmental, energy and technological issues.

This research interest is international in nature with strong participation from scientists in Asia, Europe and North America and especially students and young scientists.

The contributions in this book reflect the diversity of silicon-based materials and the new developments in the strategies and concepts at work.

The editors are especially grateful to the authors for their contributions and cooperation which made this book possible. We thank all of them for their participation.

François Ganachaud
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Part 1
Functional Polysiloxanes

New Avenues, New Outcomes: Nanoparticle Catalysis for Polymer Makeovers

Bhanu P. S. Chauhan, Bharathi Balagam, Jitendra S. Rathore, and Alok Sarkar

Abstract In this chapter, nanocluster catalyzed modifications of organic and silicon based polymers are described. The tailoring of the polymeric templates was carried out under mild conditions and led to hybrid polymers in quantitative yields. Detailed characterization studies indicated that the integrity of the polymeric templates was not compromised during the functionalization process. The nanoparticle catalysis was found to be quite effective and highly selective. In most cases exclusive ß-hydrosilylation products were obtained without any rearrangement or isomerization reactions. Detailed characterization and property profiling of the new hybrid polymers is also presented.

1 Introduction

Modern applications of polymeric materials desire and in certain instances require various functions in one family of polymeric architectures. To achieve such a goal most of the time one needs to devise new functional monomers with desired functionalities and study their polymerization to generate new polymeric materials. This approach is time tested and finally leads to desired materials. Though, one drawback to this approach is that for each new polymer a new functional monomer has to be synthesized and in certain instances new processes have to be developed to convert them to useful polymeric materials. In order to expedite the discovery of new functional polymers, one strategy could be to use a template polymer and investigate strategies to modify the property profile of such templates to achieve desired polymeric materials with required functionalities. This strategy allows a fast and efficient way to obtain functional polymeric materials in an economical fashion (Scheme 1).

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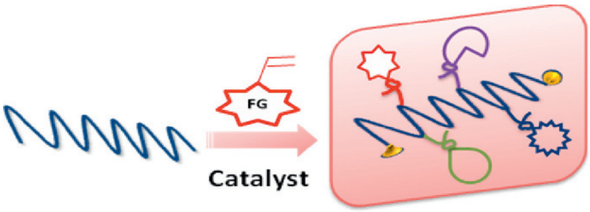


Scheme 1 Cartoon representation of polymer makeover strategy

The synthesis of mixed functionality polymers can be achieved via two types of strategies. One in which, an organic functionality is introduced into an inorganic backbone and another type could be where, inorganic or organometallic functional groups are attached to organic backbones. This type of functional group tailoring can lead to diverse family of structures, which can have desirable features and advantageous properties of both classes (organic and inorganic) of polymers. Owing to these attributes, throughout this chapter, we will use term “hybrid” to such type of polymers.

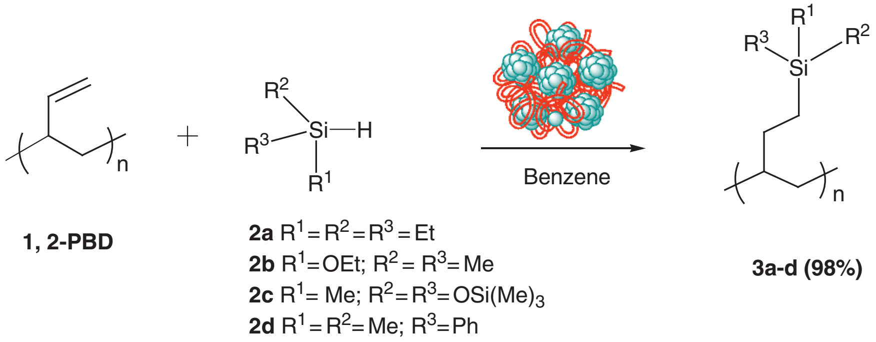
The synthesis of hybrid polymers can be regarded as an attractive avenue to develop new materials with wide-ranging desired property profiles [1, 2–7]. Recent disclosures from our laboratory have introduced new strategies for the generation of catalytically active metal nanoclusters and their utility as potent catalysts for silaesterification [8] chemo-selective hydrogenation [9] and hydrosilylation [10–13] reactions. In this chapter, we describe the strategy to generate families of new inorganic/organic hybrid polymer systems derived from hydrosilylation of polymeric templates such as polybutadienes and polyhydrosiloxane (PMHS) using various organic and inorganic functional groups.

The unsaturated polymers such as polyisoprenes and polybutadienes represent an ideal class of polymers for polymer tailoring reactions since these polymers contain one 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 weight 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, hydroformylation, hydrocarboxylation, epoxidation, oxidation, hydrosilylation and vinyl coupling reactions [1, 14–22]. In addition, a considerable number of patents have been granted on different studies of functionalization of polybutadienes. 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 silicon functionality.

2 Results and Discussion

2.1 *Tailoring of Polybutadiene Based Polymers*

In recent years, we have been investigating easy and economical functionalization of widely used carbon based polymers such as polybutadienes. The preliminary results of these studies have led our group to discover a highly selective and mild synthetic route to silyl-functionalization of 1,2-polybutadienes (PBD) via Pt-nanocluster catalyzed hydrosilylation of olefin bonds. 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 (Scheme 2).



Scheme 2 General strategy to incorporate organosilicon moiety into polybutadiene

Size exclusion chromatography (SEC) was used to determine the molecular weight and chain length properties of functionalized polymers **3a–3d** with reference to polystyrene standards (Fig. 1). The SEC chromatograms of the products have

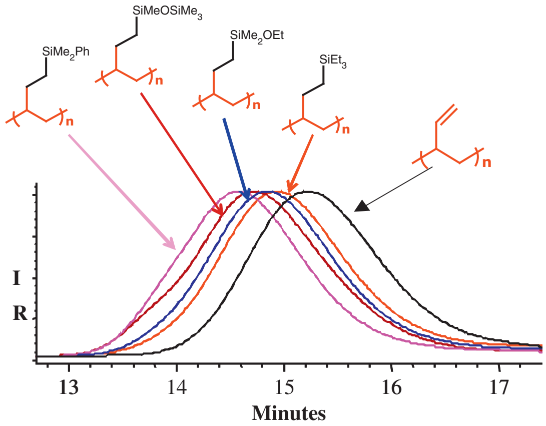


Fig. 1 SEC traces of the PBD-1 and Polymers **3a, 3b, 3c** and **3d**; mobile phase: THF (1mL/min). Taken from Ref [13]. (See also Plate 1 in the Colour Plate Section)

clearly been shifted towards the high molecular weight region, while retaining a fair molecular weight distribution ($M_w / M_n \sim 1.4$–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 large-scale molecular structure intact.

The structure and regioselectivity of these functionalized polymers **3a**–**3d** were determined by ^{1}H, ^{13}C, DEPT and ^{29}Si NMR studies. ^{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 1,2-PBD unit (β-product). Distortionless Enhancement by Polarization Transfer (DEPT) of ^{13}C NMR was used to differentiate between α and β product of hydrosilylated polymer. The selectivity towards β-product was verified for all the products by DEPT technique. For instance, the DEPT spectra of **3d** (Fig. 2) has shown one upward resonance at 33.70 which can be assigned to the methine carbon (CH) and three downward signals at 10.76, 26.72 and 37.85, were attributed to the three methylene (CH_2) carbons of polymer backbone of β-product. The opposite regioselectivity (β) would have generated two methine and two methylene carbons, lacking of which, clearly indicates the exclusive formation of α-product.

The regioselectivity of the product was further established by comparing the spectroscopic results with the hydrosilylation reaction of 1-heptene using four model silanes, **2a–2d** (Scheme 2). The ^{1}H, ^{13}C and ^{29}Si NMR results of hydrosilylation of 1-heptene (ß-product) were in good agreement with those of hydrosilylated polymers. For example, the hydrosilylation of **PBD-1** using silanes **2a, 2b, 2c, 2d** gave single ^{29}Si resonances at δ(ppm) 7.06, 18.01, 7.02/–20.36 and –1.7 respectively, which are comparable to the Si shifts observed for the hydrosilylated 1-heptene (7.7,17.46, 6.94/–21.05, –2.66). The ^{29}Si NMR, with only one detectable ^{29}Si resonance indicates the high selectivity of these reactions with exclusive formation of ß-adduct. In particular, the hydrosilylation reaction of the silane **2d** is noteworthy because this organosilane is known to favor Markovnikov product [15]. In the present catalysis under standard conditions, even silane **2d** led to formation of exclusive ß-product in quantitative yields.

To widen the scope of hydrosilylation of polybutadienes, we have screened a variety of cholorofunctional silanes, **2e**–**2i** to generate functional butadienes, which

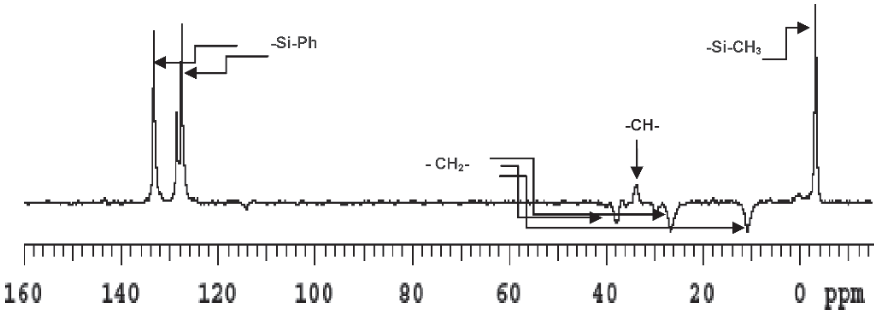
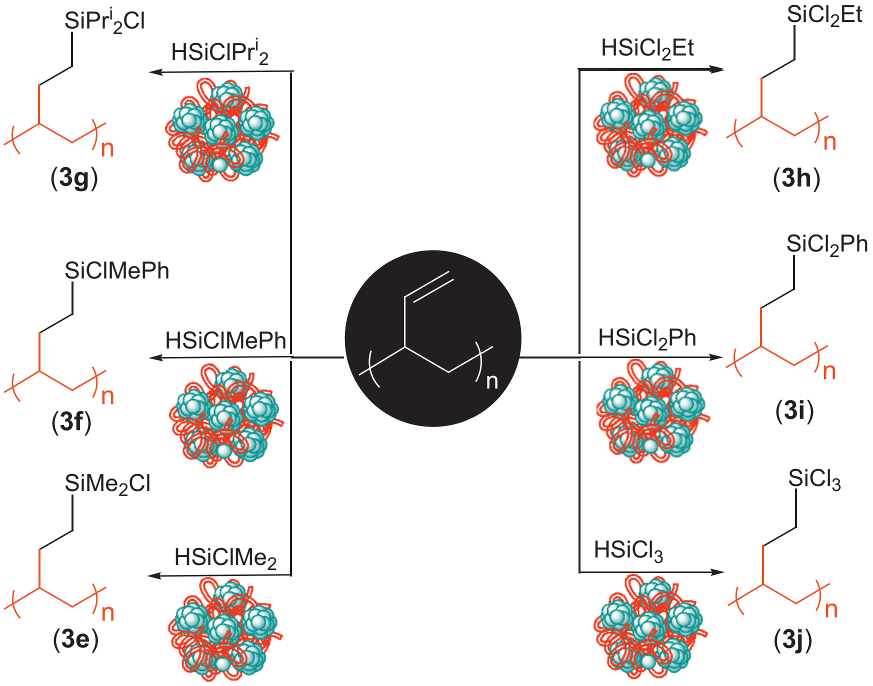


Fig. 2 ^{13}C NMR (DEPT) spectra of **3d** indicating aromatic, CH, CH_2 and CH_3 carbons



Scheme 3 Pt-nanoparticle catalyzed reaction of polybutadiene with various chlorosilanes

Table 1 Hydrosilylation of 1,2 Polybutadiene using Pt-nanoclusters

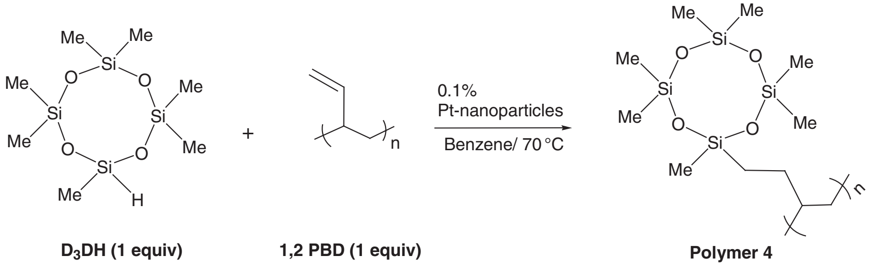
Silane Substrates	^{29}Si -NMR of silanes	Conditions [a]	Product (Yield %) [b]	^{29}Si-NMR of products
$HSiMe_2Cl$	12.2	25°C/16h	**3e** (98)	32.9
HSiPhMeCl	3.5	70°C/24h	**3f** (98)	22.1
$HSiPr^i_2Cl$	24.9	70°C/24h	**3g** (98)	36.8
$HSiCl_2Et$	13.1	45°C/24h	**3h** (98)	35.8
$HSiCl_2Ph$	−1.92	80°C/24h	**3i** (98)	20.2
$HSiCl_3$	−9.8	25°C/24h	**3j** (98)	13.5

[a] Conditions: [PBD-1] = 1.0 mmol; [silane] = 1.2 mmol; Pt-nanocluster = (0.010 gm); Solvent: Benzene,
[b] Yields are based on isolated products. The isolation was performed under nitrogen atmosphere.

after classical reactions may lead to novel polymers **3e–3i** (Scheme 3, Table 1). Almost complete functionalization (95–98%) of 1,2 vinyl groups of the polymer was achieved with variety of chloroalkyl or chloroalkylphenyl silanes. The results are summarized in Table 1. All the products have shown high yields and selectivity, regardless of the nature of the silane, as evidenced by ^{1}H, ^{13}C, ^{29}Si NMR spectroscopy (Table 1). This general trend of selectivity is very encouraging and bodes well for the commercial applications of nanoparticle catalysts.

Cyclic siloxanes are one of the important class of inorganic-organic hybrid compounds, which have often been used to improve the properties of the materials [23–25].

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 4). 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 1,2 PBD (0.056 g, 1.0 mmol) dissolved in dry benzene (2 ml) was added to the Schlenk tube 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, catalyst particles (fine powdery precipitate) were visible again, which were very conveniently separated by centrifugation (1 h). After separation of the catalysts the solvent was evaporated to obtain the product polymer **4** (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 4).



Scheme 4 Pt-Nanoparticle Catalyzed Hydrosilylation of 1, 2-polybutadiene with D_3DH

Size exclusion chromatography (SEC) was used to determine the molecular weight and chain length properties of functionalized polymers with reference to polystyrene standards. The SEC chromatograms of the products have clearly been shifted toward the high molecular weight region, while retaining a quite narrow molecular weight distribution ($Mw/Mn = 1.4$–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.

^1H, ^{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) (Fig. 3).

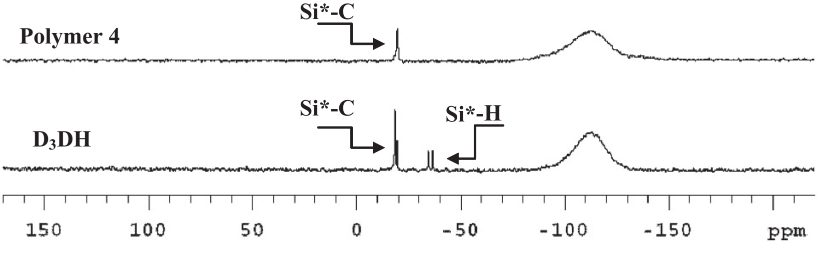
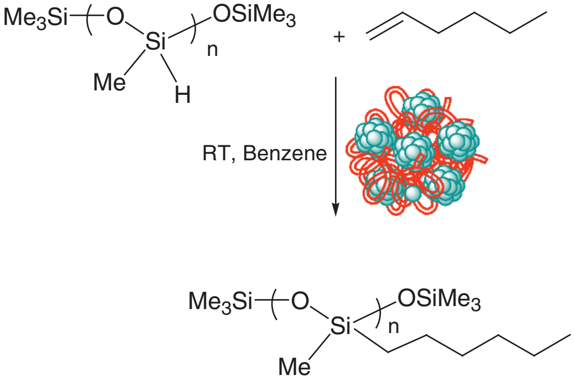


Fig. 3 Coupled ^{29}Si NMR of D_3DH and Polymer 4 showing disappearance of Si signals associated with Si centers containing Si—H bonds

2.2 Tailoring of Poly(siloxane) Based Polymers

The other type of hybrid system could be where organic functional groups are substituted on a main chain organometallic/inorganic polymer template. One of the well-established strategies is to substitute functionality via catalytic hydrosilylation reaction of alkenes. Generally, organic moieties can be covalently attached either to the siloxane polymer backbone [26] or via end grafting to polymer end groups to generate hybrid siloxane-polymers [27–30]. The choice of studying such systems is based on the utility of such polymers in applications ranging from coatings to highly sophisticated electronic materials. New selective methods to modify such polymers will lead to generation of new materials with various property profiles. Our selection of siloxane polymer for the main-chain grafting is polymethylhydrosiloxane (PMHS) because of the presence of Si-H bonds in the main chain. Moreover, commercial availability of PMHS in large scale with varying molecular weights and solubility in common organic solvent makes PMHS an ideal precursor to the functionalized organosilicon polymers (Scheme 5).



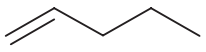
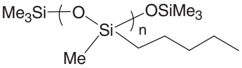
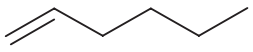
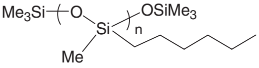
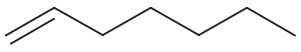
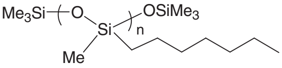
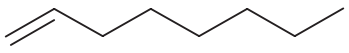
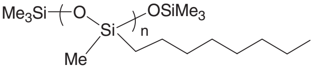
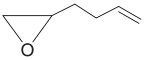
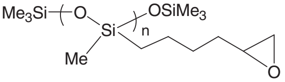
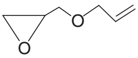
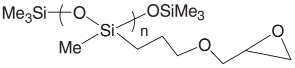
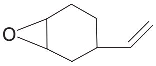
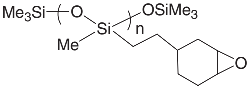
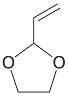
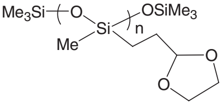
Scheme 5 Pt-nanocluster catalyzed reaction of 1-hexene with PMHS

To functionalize polymethylhydrosiloxane with organic functional groups, PMHS 1 (0.06 mL, 1.0 mmol; Mw ~ 2000 g.mol^{-1}), Pt-nanoclusters (0.01 g, 0.001 mmol Pt), and 1-hexene (0.13 mL, 1.0 mmol) were mixed together in 4-mL benzene and stirred at room temperature (Scheme 4). After 1-h of stirring, colorless reaction mixture gradually turned to homogenized brownish-yellow solution suggesting the dispersion of Pt-nanoclusters.

The progress of the reaction was monitored with ^{1}H NMR spectroscopy, which manifested gradual disappearance of peaks associated with Si-H (δ 4.58) and olefinic-protons (δ 4.8–5.9) with concomitant appearance of new peaks in the methylene region (δ 0.4–1.2). Complete disappearance of peaks associated with starting materials was observed after 20-h of the reaction. Isolation of the product was carried out by high-speed centrifugation (20 min) of reaction mixture, which led to the precipitation of Pt-nanoclusters. After separation of the catalyst, evaporation of the solvent furnished a polymer **2** (Entry 2, Table 2) as a viscous liquid. The molecular weight analysis by SEC of **2** (Mw ~ 4600 $g.mol^{-1}$ and Mw/Mn = 1.2) was consistent with the proposed structure and in good agreement with calculated value (Mw ~ 4500 $g.mol^{-1}$). ^{13}C and ^{29}Si NMR analysis of the polymer **2** was carried out to elucidate the regioselectivity of the addition reaction.

Addition of Si-H bonds to alkene can take place either in an anti-Markovnikov (β-addition) fashion resulting in silicon being attached at the terminal position or in Markovnikov (α-addition) fashion resulting in silicon bonded to the iso-position of the 1,2 alkene. Moreover, as stated in the introduction, regioselectivity of organic incorporations into the silicones was reported to play a crucial role in

Table 2 Pt-nanocluster catalyzed regioselective grafting of PMHS

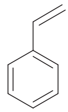
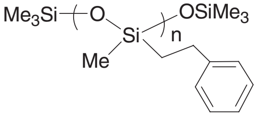
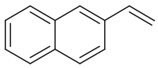
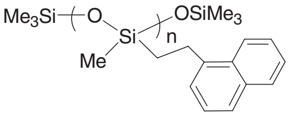
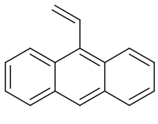
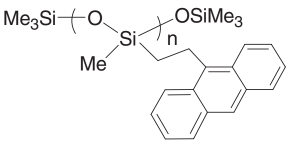
Entry	Alkene	Reaction Conditions	Product	Yield (%)
1		18h/RT		98
2		18h/RT		98
3		18h/RT		97
4		18h/RT		99
5		32h/RT		97
6		32h/RT		97
7		34h/RT		90
8		34h/RT		90

defining the property profile in terms of durability, flexibility and film toughness of the composites. ^{13}C NMR spectra of the solution revealed two new peaks at δ 23.31 (-*C*H$_2$Si) and δ 14.31 (-*C*H$_2$CH$_2$Si) respectively, indicating exclusive β-silylation of 1-hexene at terminal carbons. Furthermore, ^{29}Si NMR analysis of the reaction mixture showed only a single peak at δ –22.40 (-CH$_2$*Si*Me) corresponding to hexyl-substituted Silicon centers besides the peak at δ –7.28 originating from the terminal -*Si*Me$_3$ groups. The reaction was found to be quite general for other linear alkenes (entry **1, 3, 4**, and **5**; Table **2**) and provided corresponding β-adducts very selectively.

Hydrosilylation of functionalized olefins is often challenging due to the side reactions. For example, epoxy-containing olefins are susceptible to ring-opening polymerization and carbonyl-bearing olefins often yield a mixture of C-and O-silylated products. Using Pt nanocluster as the catalyst, epoxy and carbonyl containing olefins were silylated with PMHS without any side reactions. A high degree of regioselectivity was achieved by Pt-nanoclusters yielding >95% anti-Markovnikov adduct during the hydrosilylation of epoxy-functionalized linear olefins. Regioselectivity of the product remained unaffected (i.e. >95% anti-Markovnikov) by varying the functional groups (carbonyl, ether, and epoxide) on the olefins (Table **2**). Functionalization of PMHS with allylacetate (entry **9**, Table **2**) was also achieved selectively (>95% anti-Markovnikov) without any side reactions. In all of the cases, the substitution was either quantitative or near quantitative.

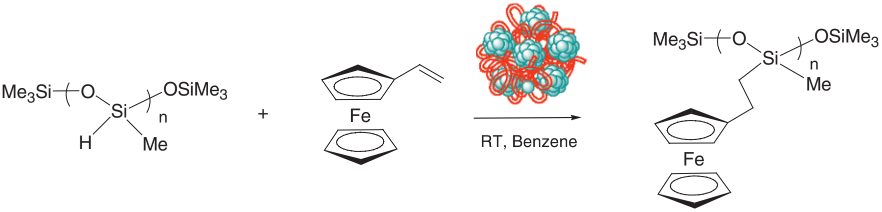
Pt-nanocluster catalyzed hydrosilylation has also been explored with aromatic alkenes using PMHS. As shown in the results summarized in Table 3, substrate dependent (alkene) regioselectivity pattern was displayed for the hydrosilylation

Table 3 Pt-nanocluster catalyzed regioselective hydrosilylation of aromatic olefins

Entry	Alkene	Reaction Conditions	Major Product	(β/α)	Yield (%)
1		48h/RT		55/45	98
2		72h/RT		65/35	98
3		78h/RT		95/5	98

of olefins containing aromatic rings (entry **1, 2, 3**; Table **3**). Hydrosilylation of styrene yielded polymer, which was a mixture of regioisomers (β/α, 55/45). An improvement in the selectivity towards β-silylated product (β/α: 65/35) was observed with 2-vinylnaphthalene (entry **2**, Table **3**). A further increase in the number of aromatic rings (entry **3**, Table **3**; 9-vinylanthracene) led to almost exclusive β-silylated polymer (entry **3**; Table **3**). Increased steric hindrance in conjunction with electronic effects of aromatic rings seems to affect the above regioselectivity pattern in the hydrosilylated product.

Metal containing polymers are a very interesting class of polymers due to their potential applications in various fields. In order to explore the possibility of incorporating metallocenes into the polymer main chain reactivity nanoparticle catalyzed hydrosilylation of PMHS was also investigated. Reaction of vinylferrocene with PMHS yielded corresponding addition product regioselectively in near quantitative yields and under moderate conditions and without any side reaction involving metallocene-ring (Scheme 6). Detailed studies are underway to compare the physical and chemical properties of metal containing polymers to investigate if regeoselective attachment of metallic functionality impacts the assembly as well as the morphology of the resulting polymers.



Scheme 6 Regiospecific addition of vinylferrocene to PMHS

3 Conclusions

In conclusion in this chapter we have described polymer makeover by reacting organic or inorganic/organometallic polymer templates with variety of functional alkenes in presence of Pt-nanoparticle catalyst. In both cases nanoparticle catalysts were very active and more importantly highly selective to provide almost exclusively anti-Markovnikov products. Thorough characterization of the resulting products indicated that the integrity of the main chain of the template polymer was unaffected during and after functionalization process.

These results also demonstrate that the template based polymer modification can be quite fruitful strategy and can lead to libraries of materials for commodity applications as well as for various sophisticated functions. Currently, we are studying comparative catalysis not only to improve the new functional group compatibility but also to explore reversal of regionselectivities and efficiencies.

4 Experimental Section

All of the experiments and manipulations were performed under nitrogen using standard Schlenk line techniques. Solvents were purchased from EM science (Merck) and distilled over sodium/benzophenone before use. PMHS (Mw ≈ 2000 g.mol^{-1}), $Me_2Pt(COD)$, polybutadienes 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. SEC 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 $2000-4\times10^6$ Å respectively. This instrument was calibrated using polystyrene standards. THF was used as an eluent at the flow rate of 1 ml/min at 40°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. The amount of Pt present in the cluster was determined on the basis of SEM data, which is ~0.001 mmol per 0.01 gm of the solid.

4.1 *Synthesis of Pt-Nanoclusters*

Me_2Pt (COD) (cod: 1,5 cyclo-octadiene) (0.25 mmol, 0.084 g), and PMHS (10.00 mmol, 0.60 mL) were added in 50 mL toluene in a 200-mL RB. Reaction mixture was stirred at 80°C for 24 h under positive pressure of nitrogen. Reduction of Me_2Pt (COD) was monitored with UV-vis spectroscopy, which revealed a gradual disappearance of peaks associated with the Me_2Pt (COD) leading to a featureless spectrum. After verifying the presence of "Pt"-nanoclusters in the solution with EM-spectroscopy, flow of nitrogen was stopped and the flask was exposed to air. Further stirring of the solution in air yielded a black gummy solid. The solid was washed thoroughly with toluene/benzene (100 mL) to remove organic moieties. Air-drying of the gummy solid furnished a black powder, which was characterized with various spectroscopic techniques and used as hydrosilylation catalyst. ^{29}Si CP/MAS δ –36.15 (D, Si-H), −81.46(T), −102.58(Q, SiO_2), −112.26(Q, SiO_2). ^{13}C CP/MAS δ –3.35 ($-SiCH_3$). FT-IR spectra (KBr, cm^{-1}) 2175 (Si-H), 1120 (Si-O-R), 1050 (Si-O-Si), 893 (Si-OH).

4.2 *General Procedure For Hydrosilylation of Polybutadienes*

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-1 (0.054 g, 1 mmol) dissolved in freshly prepared dry benzene (2 ml) was added to the Schlenk tube, followed by the addition of **2a** (0.13 ml, 1.2 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.[12] The reaction progress was monitored by ^{1}H NMR spectroscopy. On completion of the reaction, the solid catalyst was separated by centrifugation. The filtrate was evacuated to obtain the crude product. The product thus obtained was passed through the silica gel column (hexane) and analyzed by using SEC and ^{1}H, ^{13}C, DEPT, ^{29}Si NMR techniques.

4.3 Characterization of the Silylated Polybutadienes

Polymer, 3a (Scheme 2): ^{1}HNMR (CDCl$_3$, 200 MHz): δ (ppm) 0.44 (t, 9H), 0.85 (q, 6H), 0.0–2.0 (br, 7H). ^{13}CNMR/DEPT (CDCl$_3$, 200 MHz): δ (ppm) 3.29 (-Si*CH*$_2$CH$_3$), 7.52 (-SiCH$_2$*CH*$_3$), 27.0 (-*CH*$_2$CH$_2$Si), 34.7 (-*CH*CH$_2$-), 38.1 (-CH*CH*$_2$-). ^{29}SiNMR (CDCl$_3$, 600 MHz): δ (ppm) 7.76.

Polymer, 3b (Scheme 2): ^{1}HNMR (CDCl$_3$, 200 MHz): δ (ppm) −0.04 (s, 6H), 0.2–2.0 (br, 7H), 1.05 (t, 3H), 3.52 (q, 2H). ^{13}CNMR/DEPT (CDCl$_3$, 200 MHz): δ (ppm) −2.14 (-Si*CH*$_3$), 11.29 (-CH$_2$*CH*$_2$Si-), 18.305(-OCH$_2$*CH*$_3$), 25.79 (-SiCH$_2$*CH*$_2$-), 33.57(-*CH*CH$_2$-), 37.68 (-CH*CH*$_2$-), 58.16 (-O*CH*$_2$CH$_3$). ^{29}SiNMR (CDCl$_3$, 600 MHz): δ (ppm) 18.01

Polymer, 3c (Scheme 2): ^{1}HNMR (CDCl$_3$, 200 MHz): δ (ppm) 0.27 (s, 3H), 0.4–2.0 (br, 7H), 7.34 (m, 3H), 7.50 (m, 2H).^{13}CNMR/DEPT (CDCl$_3$, 200 MHz): δ (ppm) −3.22 (-Si*CH*$_3$Ph), 10.76 (-CH$_2$*CH*$_2$Si-), 26.72(-SiCH$_2$*CH*$_2$-), 33.7(-CH*CH*$_2$-), 37.85 (-*CH*CH$_2$-), 127.49 (-Si*Ph*), 128.12 (-Si*Ph*), 128.54 (-Si*Ph*), 133.3 (-Si*Ph*). ^{29}SiNMR (CDCl$_3$, 600 MHz): δ (ppm) −1.795.

Polymer, 3d (Scheme 2): ^{1}HNMR (CDCl$_3$, 200 MHz): δ (ppm) −0.10 (s, 3H), −0.02 (s, 6H), 0.0–2.0 (br, 7H). ^{13}CNMR/DEPT (CDCl$_3$, 200 MHz): δ (ppm) −0.72 (-Si*CH*$_3$OSiCH$_3$), 1.62 (-SiCH$_3$OSi*CH*$_3$), 12.93 (-CH$_2$*CH*$_2$Si-), 25.95 (-*CH*$_2$CH$_2$Si-), 33.7(-*CH*CH$_2$-), 37.96 (-CH*CH*$_2$-).^{29}SiNMR (CDCl$_3$, 600 MHz): δ (ppm) −20.36, 7.02.

Polymer, 3e (Table 1): ^{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$_2$Si-), 33.6(-*CH*CH$_2$-), 38.1 (-CH*CH*$_2$-). ^{29}SiNMR (CDCl$_3$, 600 MHz): δ (ppm) 32.97.

Polymer, 3f (Table 1): ^{1}HNMR (CDCl$_3$, 200 MHz): δ (ppm) 0.49 (s, 3H), 0.0–2.0 (br, 7H), 7.23 (m, 3H), 7.45 (m, 2H). ^{13}CNMR/DEPT (CDCl$_3$, 200 MHz): δ (ppm) 0.26 (-Si*CH*$_3$), 13.52 (-CH$_2$*CH*$_2$Si-), 25.83 (-*CH*$_2$CH$_2$Si-), 33.43 (-*CH*CH$_2$-), 37.86 (-CH*CH*$_2$-), 128.06 (-Si*Ph*), 130.27 (-Si*Ph*), 133.27 (-Si*Ph*), ^{29}SiNMR (CDCl$_3$, 600 MHz): δ (ppm) 22.17.

Polymer, 3g (Table 1): ^{1}HNMR (CDCl$_3$, 200 MHz): δ (ppm) 0.0–2 (br, 21H). ^{13}CNMR/DEPT (CDCl$_3$, 200 MHz): δ (ppm) 8.05 (-CH$_2$*CH$_2$*Si-), 13.73 (-Si*CH*(CH$_3$)$_2$), 16.99 (-SiCH(*CH$_3$*)$_2$), 25.8 (-*CH$_2$*CH$_2$Si-), 33.93(-*CH*CH$_2$-), 37.61(-CH*CH$_2$*-). ^{29}SiNMR (CDCl$_3$, 600 MHz): δ (ppm) 36.8.

Polymer, 3h (Table 1): ^{1}HNMR (CDCl$_3$, 600 MHz): δ (ppm) 0.0–2 (br, 12 H). ^{13}CNMR/DEPT (CDCl$_3$, 200 MHz): δ (ppm) 6.16 (-Si*CH$_2$*CH$_3$), 12.52 (-SiCH$_2$*CH$_3$*), 15.52 (-CH$_2$*CH$_2$*Si-), 25.37 (-*CH$_2$*CH$_2$Si-), 33.0 (-*CH*CH$_2$-), 37.7(-CH*CH$_2$*-). ^{29}SiNMR (CDCl$_3$, 600 MHz): δ (ppm) 35.84.

Polymer 3i (Table 1): ^{1}HNMR (CDCl$_3$, 200 MHz): δ (ppm) 0.0–2.0 (br, 7H), 7.39 (m, 3H), 7.62 (m, 2H). ^{13}CNMR/DEPT (CDCl$_3$, 200 MHz): δ (ppm) 16.58(-CH$_2$*CH$_2$*Si-), 25.47 (-*CH$_2$*CH$_2$Si-), 33.18 (-*CH*CH$_2$-), 37.86 (-CH*CH$_2$*-), 128.34 (-Si*Ph*), 131.66 (-Si*Ph*), 132.28 (-Si*Ph*), 133.29 (-Si*Ph*). ^{29}SiNMR (CDCl$_3$, 600 MHz): δ (ppm) 20.24.

Polymer, 3j (Table 1): ^{1}HNMR (CDCl$_3$, 200 MHz): δ (ppm) 0.4–2.0 (br, 7H). ^{13}CNMR/DEPT (CDCl$_3$, 200 MHz): δ (ppm) 20.2 (-CH$_2$*CH$_2$*Si-), 25.76(-*CH$_2$*CH$_2$Si-), 32.97 (-*CH*CH$_2$-), 37.83 (-CH*CH$_2$*-). ^{29}SiNMR (CDCl$_3$, 600 MHz): δ (ppm) 13.59.

Polymer 4 (Scheme 4): ^{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$_2$Si-), 33.66 (-*CH*CH$_2$-), 37.9 (-CH*CH$_2$*-). ^{29}SiNMR (CDCl$_3$, 600 MHz): δ (ppm) −20.096 (s).

4.4 Typical Procedure of Hydrosilylation of Olefins with PMHS

Pt-nanoclusters (0.010 g, 0.001 mmol Pt), PMHS (1.0 mmol, 0.06 mL), and 1-hexene (1.00 mmol, 0.13 mL) were mixed together in 4 mL of freshly distilled benzene in a 50-mL Schlenk-tube. Schlenk-tube was degassed three-time using standard Schlenk-tube-technique followed by stirring at room temperature. ^{1}H NMR spectroscopy was used to monitor the progress of catalytic transformation. After confirming the total substitution, product separation was carried out by high-speed centrifugation of reaction mixture (20 min), which led to precipitation of nanoclusters. Evaporation of solvent yielded pure poly(methylhexyl)siloxane. Isolation of the product was followed by multinuclear NMR spectroscopy characterization of the product.

Poly(methylpentyl)siloxane (Entry 1, Table 2): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.063, 0.51(m), 0.88(m), 1.29(m); ^{13}C NMR (CDCl$_3$, 200 MHz) δ 1.69, 14.20, 17.90, 22.65, 22.99, 35.85; ^{29}Si NMR (CDCl$_3$, 600 MHz) δ −21.83, 7.24.

Poly(methylhexyl)siloxane) (Entry 2, Table 2): ^{1}H NMR (CDCl$_3$, 200 MHz) δ −0.003, 0.46(m), 0.81(m), 1.22(m); ^{13}C NMR (CDCl$_3$, 200 MHz) δ −0.094, 2.047,14.31, 17.99, 22.90, 23.31, 31.94, 33.41; ^{29}Si NMR (CDCl$_3$, 600 MHz) δ −22.40, 7.28.

Poly(methylheptylsiloxane) (Entry 3, Table 2): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.19, 0.67(m), 0.92(m), 1.33(m); ^{13}C NMR (CDCl$_3$, 200 MHz) δ 1.28, 3.03, 15.62, 19.43, 23.54, 24.40, 30.77, 33.50, 35.11; ^{13}C NMR (CDCl$_3$, 200 MHz) δ, −21.86, 7.34

Poly(methyloctylsiloxane) (Entry 4, Table 2): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.11, 0.48(m), 0.90(m), 1.30(m); ^{13}C NMR (CDCl$_3$, 200 MHz) δ −0.32, 1.90, 14.16, 17.79, 22.86, 23.25, 29.45, 29.54, 32.14, 33.42; ^{29}Si NMR (CDCl$_3$, 600 MHz) δ −20.98, 7.00

Poly[(methyl (1,2 epoxy-5-hexane)siloxane] (Entry 5, Table 2): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.11, 0.56(m), 1.44(m), 2.31(m), 2.57(m), 2.78(m); ^{13}C NMR (CDCl$_3$, 200 MHz) δ −0.52, 17.42, 22.76, 29.38, 32.03, 46.38, 51.64; ^{29}Si NMR (CDCl$_3$, 600 MHz) δ −22.16, 7.18.

Poly[methyl(propylglycidylether)siloxane] (Entry 6, Table 2): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.07, 0.55(m), 0.88(m), 1.57(m), 2.41(m), 2.98(m), 3.24(m), 3.45(m), ^{13}C NMR (CDCl$_3$, 200 MHz) δ −0.22, 13.89, 23.72, 43.24, 50.63, 69.81, 73.92, ^{29}Si NMR (CDCl$_3$, 600 MHz) δ −21.60, 7.78.

Poly[methyl (4-ethylcyclohexyl-1, 2-epoxide)siloxane] (Entry 7, Table 2): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.25, 0.30, 0.28, 0.67, 1.22(m), 1.38 (m), 1.41(m), 1.59(m), 1.75(m), 1.85(m), 1.97(m), 2.08(m), 2.27(m), 2.34(m), 2.59(m), 3.04(m), 3.14(m), ^{13}C NMR (CDCl$_3$, 200 MHz) δ 0.28, 2.39, 13.02, 13.15, 15.06, 15.10, 21.46, 23.68, 24.23, 24.76, 25.78, 25.90, 26.65, 27.65, 30.12, 31.07, 32.35, 32.86, ^{29}Si NMR (CDCl$_3$, 600 MHz) δ −21.49.

Poly[methyl(2-ethyl-1,3-dioxolane)siloxane] (Entry 8, Table 2): ^{1}H NMR (CDCl$_3$, 200 MHz) δ −0.06, 0.06, 0.87(t), 1.07(t), 1.62(m), 3.78(m), ^{13}C NMR (CDCl$_3$, 200 MHz) δ −0.45, 8.25, 27.26, 66.65, 73.16, 106.08, ^{29}Si NMR (CDCl$_3$, 600 MHz) δ −21.94, 7.80.

Poly[methy(ethylphenyl)siloxane] (mixture of β:α products) (Entry 1, Table 3): ^{1}H NMR (CDCl$_3$, 200 MHz) δ −0.07(m), 0.76(m), 1.28(m), 2.56(m), 6.6(m), 7.2(m), 7.56(m); ^{13}C NMR (CDCl$_3$, 200 MHz) δ 1.2, 1.8, 14.8, 19.5, 29.1, 30.7, 113, 124, 125, 126, 127, 128, 137, 144; ^{29}Si NMR (CDCl$_3$, 600 MHz) δ −26.1, −22.2.

Poly[methyl (2-ethylnapthalene)siloxane] (Entry 2, Table 3): ^{1}H NMR (CDCl$_3$, 200 MHz) δ −0.008, 0.84(m), 1.37(m), 2.21(m), 2.67(m), 6.80(m), 6.90(m), 7.30(m), 7.54(m), ^{13}C NMR (CDCl$_3$, 200 MHz) δ −0.19, 1.32,14.81,19.11, 29.17, 30.95, 123, 125.13, 126.93, 127.68, 128.46, 129.67, 131.72, 132.10, 133.90, 141.99, ^{29}Si NMR (CDCl$_3$, 600 MHz) δ −25.79, −21.72.

Poly[methyl (9-ethylanthracene)siloxane] (Entry 3, Table 3): ^{1}H NMR (CDCl$_3$, 200 MHz) δ 0.43, 1.37(m), 1.62(t), 3.80(q), 7.33(m), 7.55(m), 7.70(m), 8.13(m), 8.45(m), 8.55(m), ^{13}C NMR (CDCl$_3$, 200 MHz) δ 2.51, 15.94, 21.51, 123.21, 125.51, 125.78, 126.43, 126.85, 129, 71, 130.23, 131.89, 132.03, 133.99, 137.00, ^{29}Si NMR (CDCl$_3$, 600 MHz) δ −21.45 (broad).

Poly[methy(2-ethylferrocene)siloxane] (Scheme 6): ^{1}H NMR (CDCl$_3$, 200 MHz) δ −0.047, 0.041, 0.74(m), 1.14(m), 1.49(m), 2.23(m), 4.00 ^{13}C NMR (CDCl$_3$, 200 MHz) δ −0.16, 14.09,18.83, 22.69, 26.77, 67.12, 67.55, 68.39, 91.83, ^{29}Si NMR (CDCl$_3$, 600 MHz) δ −21.97 (broad).