SYNTHESIS, REACTIVITY AND MICROSTRUCTURE OF POLYSILANES BEARING CARBOSILYL SIDE CHAIN SUBSTITUENTS

by

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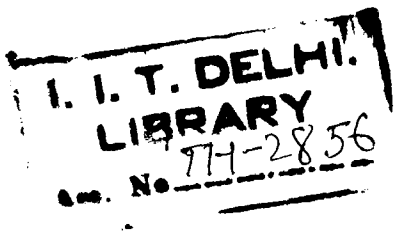

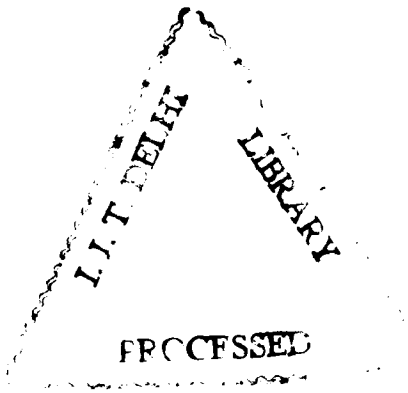

CERTIFICATE

This is to certify that the thesis entitled, " Synthesis, Reactivity and Microstructure of Polysilanes Bearing Carbosilyl Side Chain Substituents", being submitted by Mr. Anubhav Saxena to Indian Institute of Technology, Delhi for the award of the Degree of Doctor of Philosophy, is a record of bonafide research work carried out by him. Mr. Anubhav Saxena has worked under my supervision and guidance and has fulfilled all the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results embodied in this thesis have not been submitted, in part or in full to any other University or Institute for the award of any degree or diploma.

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(ANUBHAV SAXENA)

ABSTRACT

The work embodied in the present thesis is aimed at synthesis of hitherto unknown polysilanes bearing functional carbosilyl side chains. The interest in these polysilanes stems from a desire to expand the scope of reaction chemistry in the side chain substituents as well as to explore the $^{29}Si\{^{1}H\}$NMR response of carbosilyl silicon atoms in extracting the configurational information of these polysilanes. The results emerging from these studies are described in chapters 3-5.

Chapter 3 is divided into two sections. Section A describes the synthesis and characterization of some hitherto unknown carbosilanes bearing primary and /or tertiary SiH groups. Section B deals with the studies on catalytic dehydropolymerization of these monomers which afford new functional polysilanes.

The synthesis of carbosilane monomers **1a-4a** (equation 1) involves hydrosilylation reaction between appropriate hydrosilane and trichlorovinylsilane and subsequent treatment of the resulting chlorocarbosilanes with lithium aluminum hydride. Various factors including temperature, catalyst concentration and reaction time have been studied to promote the formation of the desired carbosilanes.

$$CH_2{=}CHSiCl_3 + R^1R^2R^3SiH \xrightarrow[\text{(ii) } LiAlH_4]{\text{(i) } H_2PtCl_6} \underset{\textbf{1a-4a}}{R^1R^2R^3Si(X)\,SiH_3} \qquad (1)$$

X= $-CH_2CH_2-$ (β- isomer) ; $-CH(CH_3)-$ (α - isomer)

$R^1 = H, R^2 = Me, R^3 = Ph$ (**1a**);

$R^1 = H, R^2, R^3 = Ph$ (**2a**);

$R^1 = H, R^2, R^3 = Me$ (**3a**);

$R^1, R^2, R^3 = Et$ (**4a**).

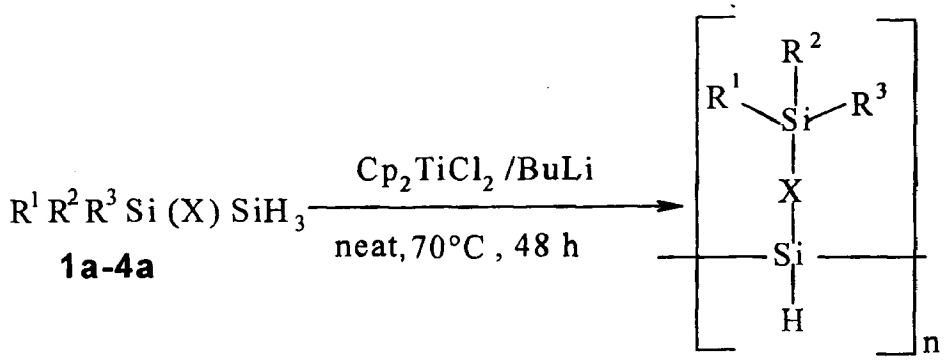
The compounds **1a-4a** are colorless, distillable liquids and are obtained as a mixture of α- and β- isomers. Though Speier's catalyst is quite effective to bring about hydrosilylation of the appropriate organosilicon reagents, attempts to synthesize predominant α- or β- addition product were not successful under the reaction conditions employed.

These carbosilanes have been characterized by IR and multinuclear NMR studies. ^{1}H NMR spectrum of each carbosilane allows the detection of both α- and β- isomers which is further confirmed by $^{13}C\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR spectra. The spectroscopic data for **1a** reveals the presence of two diastereomers of the α addition product. ^{1}H NMR spectrum exhibits doublet of doublets centered at δ 0.38 and 1.15 due to HSi*Me* and C-*CH*$_3$ protons respectively and suggests the presence of diastereomers by virtue of adjacent chirality at Si and C centers. In accord with the ^{1}H NMR data, $^{13}C\{^{1}H\}$ NMR spectrum of **1a** reveals two signals each for CH (δ -4.05,-4.31) and CH_3(δ 12.01, 12.62) carbons associated with the diastereotopic α-isomers. $^{29}Si\{^{1}H\}$ NMR spectrum of **1a** reveals three distinct signals each in the region, δ -7.3 to –11.2 and -53.0 to -54.2. The former values are ascribed to PhMe*Si*H moiety while the latter to H_3Si group. The detailed assignments of ^{1}H, $^{13}C\{^{1}H\}$, $^{29}Si\{^{1}H\}$ NMR signals are made on the basis of DEPT 135/90, TOCSY and HSQC NMR experiments.

The carbosilanes **1a-4a** serve as useful precursors for the synthesis of polysilanes bearing functional carbosilyl side chains. The synthetic method involves the catalytic dehydrocoupling of the corresponding monomers using the previously known catalyst, Cp_2TiCl_2/BuLi. It is noteworthy that these reactions proceed selectively at the primary Si-H site while tertiary Si-H group remains inert during polymerization. This selective transformation leads to functionally substituted carbosilyl side chains on the catenated silicon backbone (Scheme 1). The separation of small amounts of cyclic and low molecular weight species from the crude polymers is effected with repeated solvent extraction using pentane-methanol mixture. The polymers thus obtained are soluble in common organic solvents such as dichloromethane, chloroform, hexane, toluene, tetrahydrofuran etc. GPC data of these polymers show a monomodal molecular weight distribution with $\overline{DP}$ ranging between 12-35 and polydispersity 1.4-1.7. IR, ^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR coupled with detailed 2D NMR experiments allows the structural elucidation of these polysilanes.

^1H NMR spectrum of each polysilane in $CDCl_3$ shows broad unresolved massifs in the regions characteristic of functional group protons. For **1-3**, different Si-H protons associated with the pendant carbosilyl unit and the skeletal framework are identified by ^1H, $^{29}Si\{^1H\}$ and $\{^1H\text{-}^{29}Si\}$ HSQC NMR spectroscopy. In ^1H NMR spectra of the polysilanes **1** and **2**, the pendant and skeletally bound Si-H groups appear at δ 4.22-4.85 and 3.35-3.78 respectively in nearly 1:1 ratio. This precludes the possibility of cross-linking reactions during dehydropolymerization. For **3**, a fortuitous chemical shift overlap of

the Si-H groups is observed at δ 3.3-3.8. The spectral data is consistent with the idealized structure of the polymers as shown in scheme 1.



1-4

X= -CH_2CH_2- and –$CH(CH_3)$-;

R^1 = H, R^2 = Me, R^3 = Ph (**1**); R^1 = H, R^2 = R^3 = Ph (**2**);

R^1 = H, R^2 = R^3 = Me (**3**); R^1 = R^2 = R^3 = Et (**4**).

Scheme-1

DEPT 135 $^{29}Si\{^1H\}$ spectra reveal complex pattern of signals in the region of δ -7.8 to –11.9 and –52.5 to – 67.0. The former chemical shift values are attributed to silicon atoms of the pendant carbosilyl units by comparison with those of the precursors, while the later values are ascribed to the skeletal silicon atoms. It is imperative to mention that the broad and complex $^{29}Si\{^1H\}$ NMR spectral pattern of backbone Si-H as observed for **1-4** is a common feature for other known poly(hydrosilane)s obtained from the catalytic dehydrocoupling pathway. This is believed to arise from the adjacent stereogenic silicon atoms and also the higher order of sequencing in these polysilanes. A comparison of the $^{29}Si\{^1H\}$ NMR spectra in

DEPT 135 and normal modes reveal similar spectral characteristics. This implies that further cross-linking of Si-H groups in the linear structure is either not present or is too weak to be detectable in $^{29}Si\{^{1}H\}$ NMR spectrum. Quantitative $^{13}C\{^{1}H\}$ NMR spectra apparently reveal the presence of both α- and β- carbosilane side chains nearly in the same ratio as observed in the parent carbosilanes.

UV spectra of **1-4** in dichloromethane solution show absorptions at 262-265 nm due to σ bond delocalization in the skeletal framework. In the IR spectra, a strong absorption at ca. 2110-2118 cm^{-1} due to νSi-H mode is lowered by 30-40 cm^{-1} as compared to that of carbosilane monomers.

The results of thermogravimetric analysis (TGA) reveal that onset of thermal decomposition of the least stable polysilane **4** begins at 110°C while the polysilane **2** is stable up to 350°C. The thermal stability of **1** and **3** lies between these two extremes. The residual yields are found to vary between 45-74%. It is evident that the onset of thermal decomposition as well as the residual yield depend upon the nature of functionalities at the carbosilyl ends. Although a detailed study of the thermal decomposition pathway is warranted, the observed high residual yield indicates the potential of these polymers as preceramic precursors.

Following the synthesis of polysilanes **1-4**, studies have been extended to understand the chemical reactivity of these polysilanes. The reactivity behavior of Si-Ph/Si-H groups present in these polymers has been examined towards various electrophilic and nucleophilic substituents (chapter 4).

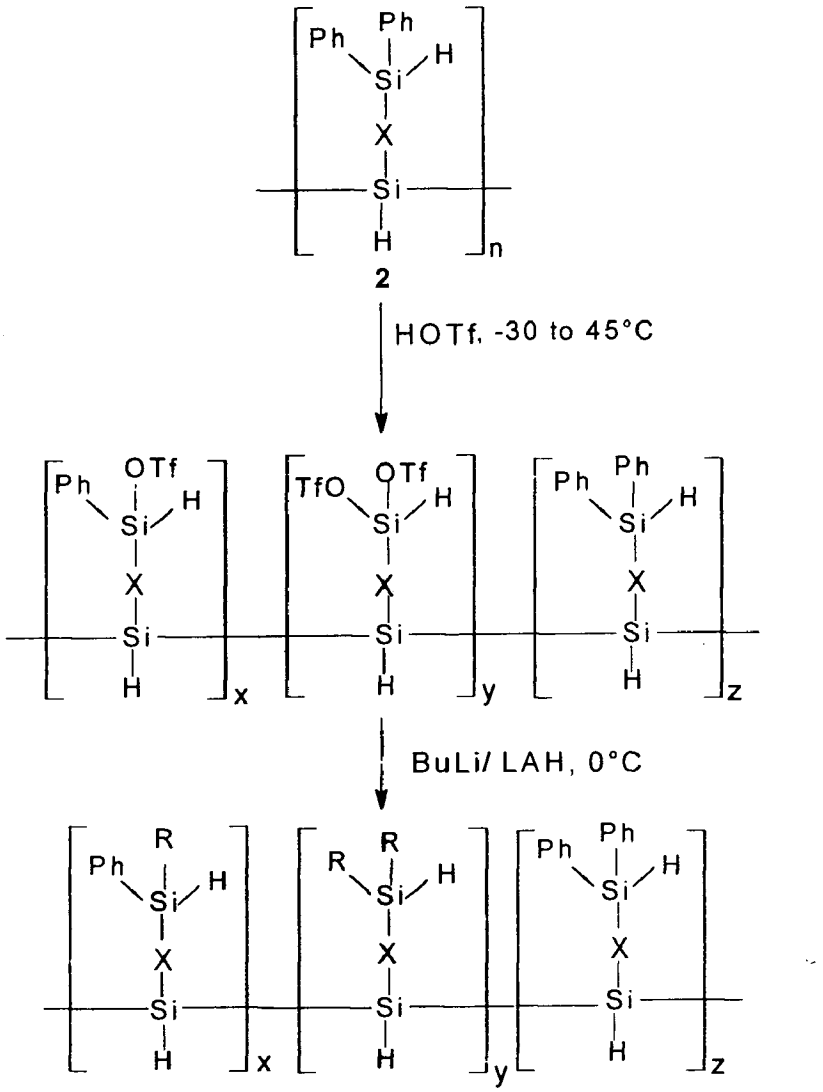
The polymers $-[R^1R^2R^3SiXSiH]_n$ (R^1 = Ph, R^2 = Me, R^3 = H (**1**); R^1 = R^2 = Ph, R^3 = H(**2**); X = $-CH_2CH_2-$ and $-CH(CH_3)-$) are subjected to chemical modification at the carbosilyl side chains. The general approach followed is the dearylation of Si-Ph bonds by triflic acid to generate the reactive Si-OTf species and subsequent reactions with nucleophilic substrates such as BuLi, $LiAlH_4$ or MeLi. Such studies when carried out on the polymer **1** afford new carbosilyl substituted polysilanes $-[RMeHSiXSiH]_n$,(R = Bu (**1b**); H (**1c**); Me (**1d**)). A detailed ^1H NMR spectral study of these reactions at different interval reveals that ~97% conversion of Si-Ph to Si-OTf takes place in 3h. In the ^1H NMR spectrum, the retention of Si-H (carbosilyl), Si-H (backbone) and Si-CH_3 groups in desired concentration was clearly evident from the resonances at δ 4.30-4.68, 3.51-3.78 and 0.38 respectively. The chemical shift values of the Si-H protons are found to be quite sensitive to the variation of functional groups at the carbosilyl silicon atom (RMeHSi) (Table-1). These new polymers are characterized by GPC, IR, ^1H, $^{13}C\{^1H\}$, $^{29}Si\{^1H\}$ as well as (^1H-^{29}Si) HSQC NMR spectroscopy.

Table 1

Carbosilyl groups (RMeHSi)	δ ^1H (ppm)
1. PhMeSiH	4.25-4.60
2. BuMeSiH	3.31-3.82
3. $MeSiH_2$	3.37-3.70
4. Me_2SiH	3.32-3.92

On the other hand, Si-Ph groups of polysilane **2** react with either 1.0 or 2.0 equivalents of triflic acid in a non-selective manner. The isolation of the polysilanes **2b-2e** (Scheme 2) clearly suggest that the dearylation of Si-Ph bonds with 1.0 equivalent of triflic acid does not lead to exclusive one bond Si-Ph cleavage /unit monomer. Instead, a competitive cleavage of both Si-Ph groups takes place concomitantly. Depending upon the stoichiometry of the triflic acid used, the product composition of the resulting polysilanes differs. ^{1}H NMR spectra of these polysilanes reveal that approximately 90% cleavage of Si-Ph bonds occurs with 2.0 equivalents of triflic acid. However complete dearylation of Si-Ph bonds in polysilane **2** could not be achieved since higher concentration of TfOH (> 2.1 equivalent) results in the cleavage of the skeletal backbone. The idealized structure of each polysilane has been supported by multinuclear (^{1}H, $^{13}C\{^{1}H\}$, $^{29}Si\{^{1}H\}$) NMR as well as by 2D NMR spectral studies.

It is interesting to note that the formation of silyl triflate follows the selective dearylation step while other functionalities such as Si-H and Si-Me are inert under the conditions employed. In addition, a comparison of GPC data of these polysilanes with that of the precursors is suggestive of the retention of skeletal silicon framework. This may suggest that the dearylation step which occurs remote to the skeletal backbone may be advantageous and selective as compared to the similar reactions at poly(phenylsilane)s where the chain scission phenomena is invariably observed.



Where X = $-CH_2CH_2-$ or $-CH(CH_3)-$

R = Bu (**2b**, **2c**)

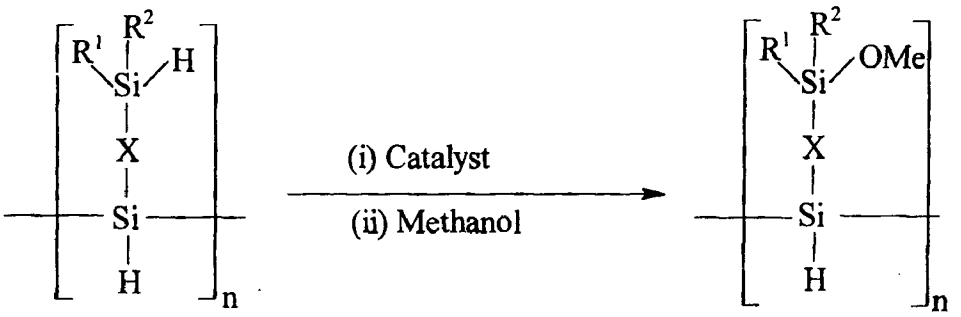
= H (**2d**, **2e**)

Scheme -2

Since the classical organic bases are known to catalyze Si-H to Si-OMe groups at the molecular level, the feasibility of similar transformation in the polysilanes **1-3**

has been attempted to draw a comparison of reaction chemistry between the classical and polymeric Si-H entities present in the polysilanes. Base catalyzed methanolysis of Si-H groups in polysilanes **1-3** have been studied in presence of biguanide, triethylamine or pyridine base as catalyst (Scheme 3). The progress of each reaction was followed by the ^{1}H NMR spectra at different time intervals. It is observed that the Si-H signals of pendant carbosilyl units slowly decrease in intensity with time and finally disappear in 4-5h while the skeletal Si-H groups remain inert. The new signals due to the Si-OMe groups (broad and complex) appear at δ 3.4-3.7. The biguanide-catalyzed methanolysis of polysilanes **1-3** reveal a quantitative conversion of side chain Si-H to Si-OMe groups, yielding the polysilanes $[R^{1}R^{2}(OMe)SiXSiH]_{n}$, (**1x-3x**) under mild conditions. Although, the rate of methanolysis of Si-H groups is found to be extremely slow (6-18% in 12h) with triethylamine or pyridine base as the catalyst, the chemoselective methanolysis of carbosilyl Si-H groups is also observed in these reactions too. In order to further confirm the chemoselective behavior of carbosilyl Si-H groups, similar reaction in presence of biguanide base was performed on the polysilane, $[Et_3Si\text{-}X\text{-}SiH]_n$, **4** (X = $-CH_2CH_2-$ and $-CH(CH_3)-$). The results obtained clearly reveal only < 5% transformation of the skeletal SiH groups in 24h. The new methoxy substituted polysilanes, **1x-3x** have been characterized by GPC, IR, ^{1}H, $^{29}Si\{^{1}H\}$ NMR as well as (^{1}H-^{29}Si) HSQC NMR data. $^{29}Si\{^{1}H\}$ NMR chemical shifts of these polysilanes, **1x-3x** show a close resemblance with those of parent polysilanes. Such chemical shift equivalence is however consistent with literature trends for analogous substituted silicon species. GPC analyses of **1x-3x** reveal a monomodal

molecular weight distribution almost similar to that of precursor polysilanes **1-3**, suggesting that skeletal silicon chain does not undergo scission during methanolysis. Similar reactions of **1-3** with other alcohols (EtOH, CF_3CH_2OH) are relatively slow under base catalyzed conditions and only 18-33 % conversion of carbosilyl Si-H to Si-OR groups can be achieved.



1-3 **1x-3x**

Catalyst = triethylamine, pyridine and biguanide

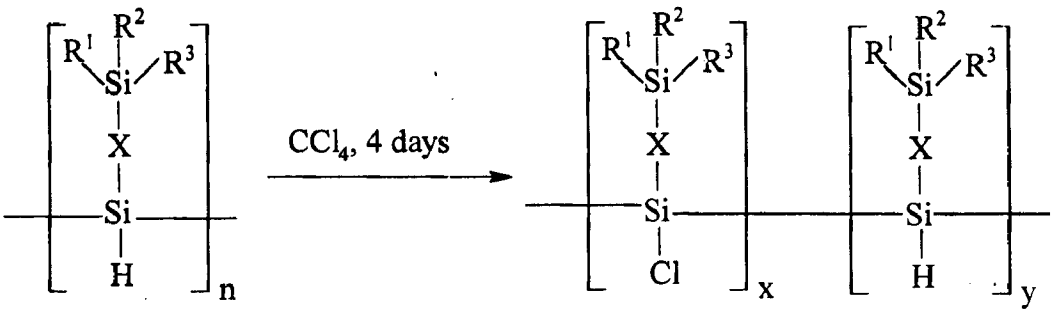
X= $-CH_2-CH_2-$ and $-CH(CH_3)-$

R^1 = Ph, R^2 = Me (**1,1x**); R^1, R^2 = Ph (**2,2x**); R^1, R^2 = Me (**3,3x**).

Scheme- 3

In contrast, the polysilanes **1-4** upon reaction with CCl_4 undergo selective free radical halogenation of the skeletal Si-H groups at room temperature while the carbosilyl Si-H groups remain unaffected (Scheme 4). ^1H NMR spectra of the resulting chlorosubstituted polysilanes **1y-4y** suggest approximately 74–78% conversion of skeletally bonded Si-H to Si-Cl groups in 4 days. The $^{29}Si\{^1H\}$ NMR spectra strongly support the identity of different silicon species present in these polymers. The spectrum

reveals two distinct spectral regions between δ 7.0 to −11.8 and 0.3 to 4.9 which are ascribed to carbosilyl silicon atoms ($R^1R^2R^3Si$) and Si-Cl containing backbone respectively. $^{29}Si\{^1H\}$ NMR signals of the residual Si-H containing species are not observed presumably due to random distribution of the remaining Si-H groups. All the chemically modified polysilanes obtained above have been characterized by IR, ^1H and $^{29}Si\{^1H\}$ NMR spectroscopy as well as GPC.



1-4 **1y-4y**

X= $-CH_2-CH_2-$ and $-CH(CH_3)-$

R^1 = Ph, R^2 = Me, R^3 = H (**1**,**1y**);

R^1, R^2 = Ph, R^3 = H (**2**,**2y**);

R^1, R^2 = Me, R^3 = H (**3**,**3y**)

R^1, R^2, R^3 = Et (**4**,**4y**)

Scheme-4

In chapter 5, the synthesis of a few polysilanes $\{R_2R^1Si(CH_2)_2SiH\}_n$ (R = Me, R^1= H (**5**); R = R^1 = Et (**6**); R = Me, R^1= Ph (**7**)) is achieved by the Cp_2TiCl_2/BuLi catalyzed

dehydropolymerization of the monomeric carbosilanes $R_2R^1Si(CH_2)_2SiH_3$. The monomers are synthesized exclusively as β-addition products by using the Karstedt's catalyst during hydrosilylation reactions between the appropriate silicon reagents.

An examination of $^{29}Si\{^1H\}$ NMR spectra of the polysilanes **5-7** indicates a broad and complex pattern of signals due to the backbone. On the other hand, the signals associated with the dangling carbosilyl side chains are quite distinct and well resolved. The microstructure of these polysilanes has been studied by analysis of $^{29}Si\{^1H\}$ NMR signals associated with side chain carbosilyl groups. On the basis of deconvolution of $^{29}Si\{^1H\}$ NMR signals, the unit intensity ratio of triad level domains (mm: mr/rm: rr) has been deduced. The validity of the parent triad assignments has been examined in terms of Bernoullian statistical model. For **5** and **6**, an excellent agreement is observed between the concentration ratio of the triad level parent peaks (from the deconvoluted $^{29}Si\{^1H\}$NMR spectrum) and those calculated on the basis of Bernoullian statistical model (Table 2). For the polysilane **7**, the spectral pattern is inconsistent with the Bernoullian statistical model of different triad sequences presumably due to the overlapping of signals associated with these triad domains.

The probability of racemic replication, (P_r) is observed as 0.82 for **5** and 0.84 for **6**. These values are significantly less than idealized value (>0.95) expected for a completely stereoregular configuration. On the basis of these data, it may be speculated that microstructure of these polysilanes have atactic configuration with a strong bias towards syndiotactic character. Determination of the microstructure of these polymers using $^{29}Si\{^1H\}$ NMR studies of side chain silicon atoms is unprecedented and offers a

quite simple and alternative approach for deducing the microstructure in related polysilanes. The validity of this method needs to be strengthened by correlating these data with those obtained from $^{29}Si\{^{1}H\}$ NMR analysis of the polymer backbone.

Table 2: Experimentally and statistically determined triad concentration ratio for 5 and 6.

Polymer	Triads	Experimentally found unit ratio	Statistically calculated unit ratio	P_m	P_r
5	rr	0.68	0.68	0.18	0.82
	mr/rm	0.28	0.29		
	mm	0.04	0.03		
6	rr	0.70	0.70	0.16	0.84
	mr/rm	0.27	0.27		
	mm	0.02	0.03		

Glossary of Symbols and Abbreviations

%	percent
δ	chemical shift
°C	degree centigrade
Ar	aryl
Bu	n-butyl
BuLi	butyl lithium
COSY	Correlation Spectroscopy
Cp	cyclopentadienyl
Cp*	pentamethyl cyclopentadienyl
d	doublet
dd	doublet of doublet
DEPT	Distortionless Enhancement by Polarization Transfer
Dp	degree of polymerization
EBI	ethylenebis(indenyl)
e.g.	for example
Eq	equation
Et	ethyl
g	gram
GPC	Gel Permeation Chromatography
h	hour
Hex	hexyl

HSQC	Heteronuclear Single Quantum Correlation
Hz	hertz
Ind	indenyl
IR	Infrared
J	coupling constant
$LiAlH_4$	lithium aluminum hydride
m	multiplet
ms	milli second
Me	methyl
MeLi	methyl lithium
min	minute
mmol	milli mole
mol	mole
M_w	weight average molecular weight
nm	nano metre
NMR	Nuclear Magnetic Resonance
PD	polydispersity
Ph	phenyl
ppm	parts per million
Pr	n-propyl
Red Al	wt % solution of sodium bis(2-methoxyethoxy) aluminium hydride in toluene
ROP	ring opening polymerization

t	triplet
t-Bu	tertiary butyl
TfOH	trifluoromethanesulphonic acid
TGA	Thermogravimetric analysis
THF	tetrahydrofuran
TMS	tetramethylsilane
TOCSY	Total Correlation Spectroscopy
UV	Ultra Violet

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