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# Synthesis of polysilanes bearing pendant carbosilyl groups and $^{29}$Si-NMR probe on the tacticity using side chain silicon atoms

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## Abstract

New functional polysilanes $[R_2R^1Si(CH_2)_2SiH]_n$ (R = Me, $R^1$ = H (**1**); R = $R^1$ = Et (**2**); R = Me, $R^1$ = Ph (**3**)) bearing carbosilyl side chains have been synthesized by catalytic dehydropolymerization of precursor carbosilanes $R_2R^1SiCH_2CH_2SiH_3$ using $Cp_2TiCl_2$–BuLi as a catalyst. These polymers are characterized by $^1H$, $^{13}C$, $^{29}Si$, $\{^1H–^{29}Si\}$ HSQC NMR spectroscopy, GPC and TGA. Attempts to delineate the tacticity from the analysis of deconvoluted $^{29}Si\{^1H\}$-NMR signals associated with the side chain silicon atoms reveal that the triad concentration ratio follows a Bernoullian statistical model for polymers **1** and **2** only.

*Keywords:* Carbosilane; Hydrosilylation; Dehydropolymerization; Microstructure; Deconvolution

## 1. Introduction

In the past two decades, there have been extensive studies on the multifaceted chemistry of linear polysilanes. By virtue of the σ bond delocalized backbone, these polymers exhibit many useful physical properties which allow their potential technical applications as photoconductors, electrical conductors, photoresists and non-linear optical materials [1].

Polysilanes are also known as excellent precursors for SiC ceramic fibers [2].

The most common approach for the synthesis of poly(dialkyl/arylsilane)s involve thermal [3], ultrasonic [4] or electrochemical [5] Wurtz coupling of dichloroorganosilanes in presence of alkali metals. Though this method results in high molecular weight polysilanes, the severe polymerization conditions impair the use of monomers with functionalized groups as well as control on average molecular weight and stereoselectivity during the chain growth [1a,1b,6]. Following the pioneering work of Harrod et al. [7], an alternate synthetic approach involving the transition metal mediated dehydrocoupling of primary organosilanes has been actively pursued. A variety of chiral and achiral Group 4 metallocene complexes have been examined as precatalysts in an attempt to improve the molecular weight and induce stereoregularity in the polymer chain [8].

It is well recognized that the intriguing electronic properties of polysilanes associated with delocalized σ bonded backbone are influenced by average molecular weight [9], nature of the substituents [10] and conformation of the polymer chain [11]. Also, the microstructure of polysilanes derived from prochiral monomer is under investigation to better understand structure–property relationship, by analogy with the stereoregular organic polymers [12]. From the analysis of deconvoluted $^{29}$Si-NMR spectra, Jones et al. [13] have reported a logical explanation of tacticity by identifying the isotactic, syndiotactic and atactic triad sequences of poly(dialkyl/arylsilane)s synthesized by Wurtz coupling. The results are found to be in accord with Bernoullian statistical model. By the similar approach, Corey et al. have recently reported a detailed analysis of complex $^{29}$Si-NMR spectra of poly(phenylsilane) [8h,8j] and poly(*p*-tolylsilane) [8k] produced by Group 4 metallocene catalyzed dehydrocoupling. It is concluded that these polymers adopt atactic configuration irrespective of the nature of the catalyst used. For poly(*p*-tolylsilane), $^1$H-NMR spectral region of methyl groups of *p*-tolyl substituents has also been examined to gauge the polymer tacticity and the results are in accord with those obtained from $^{29}$Si-NMR spectrum. In a separate study,

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Harrod et al. [8g] have made a detailed analysis of $^{29}$Si-NMR spectrum of poly(phenylsilane). In contrast to the earlier reports [8b,8e], it was observed that the nature of the dehydropolymerization precatalyst had little influence on the stereochemical outcome of the coupling reactions and predominantly atactic microstructure was concluded.

In an earlier report, Corriu et al. [2e,2f] have studied the condensation reaction of 1,4-disilapentane, $H_2MeSiCH_2CH_2SiH_3$ in presence of $Cp_2TiMe_2$ or $Cp_2TiCl_2$–2-*n*-BuLi as catalyst. The studies reveal the initial formation of oligosilane $[H_2MeSiCH_2CH_2SiH]_n$ by virtue of preferential reactivity of $SiH_3$ group. Thereafter side chain $SiH_2$ groups of the oligomer undergo condensation resulting in crosslinked polymer. Our interest in functional polysilanes bearing the carbosilyl side chains stems from a desire to expand the scope of reaction chemistry in the side chain substituents as well as to explore the $^{29}$Si-NMR response of carbosilyl silicon atoms in extracting the configurational information of these polysilanes. As a logical extension of our earlier work [14], we have synthesized new polysilanes $[R_2R^1Si(CH_2)_2SiH]_n$ ($R = Me$, $R^1 = H$ (**1**); $R = R^1 = Et$ (**2**); $R = Me$, $R^1 = Ph$ (**3**)) and studied the $^{29}$Si-NMR spectra in the region of dangling carbosilyl functional groups to understand the microstructure. The results are reported herein.

## 2. Results and discussion

### 2.1. Synthesis of monomer *1a–3a*

Hydrosilylation reaction between equimolar quantities of vinyltrichlorosilane and chlorodimethylsilane–triethylsilane–dimethylphenylsilane in presence of Karstedt's catalyst [15] results in the isolation of the corresponding chlorocarbosilanes as colorless, distillable liquids. Subsequent treatment of these derivatives with lithium aluminium hydride affords the desired carbosilane monomers **1a**–**3a** (equation 1).

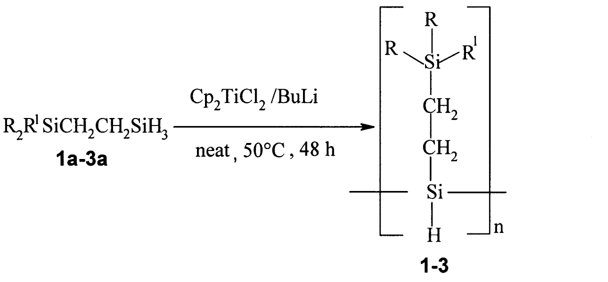
$$CH_2{=}CHSiCl_3 + R_2R^1SiH \underset{LiAlH_4}{\overset{Catalyst}{\rightarrow}} R_2R^1SiCH_2CH_2SiH_3 \qquad (1)$$

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

$^1$H, $^{13}$C and $^{29}$Si-NMR spectral data are in conformity with these compounds and suggest the formation of exclusive β- isomers during hydrosilylation. For **1a**, the $^1$H-NMR spectrum reveals two distinct signals at $\delta$ 3.87 and 3.55 in 1:3 intensity ratio and are attributed to Si–H and $SiH_3$ protons, respectively. The spectral assignments of different $-CH_2-$ groups are made in accordance with the trends reported earlier for analogous carbosilanes [14]. The $^{29}$Si-NMR spectrum of each compound exhibits two distinct signals and allows the detection of $SiH_3$ and $R_2R^1Si-$ groups (Section 3).

### 2.2. Polymerization of *1a–3a*

The neat carbosilane monomers **1a**–**3a** are subjected to dehydropolymerization using catalyst $Cp_2TiCl_2$–BuLi with 1:2.2:40 catalyst to silane ratio. The contents upon heating at 50 °C for 48 h are transformed into immobile viscous gums. Isolation of crude polymers is effected by dissolving the contents in hexane and deactivating the catalyst in air until the color of the solution changes from blue to yellow. The cyclic and low molecular weight species formed during the reactions (as evident from the $^1$H-NMR signals at $\delta$ 4.8–5.1 due to Si–H protons) are separated by repeated solvent extraction using *n*-pentane–methanol mixture. The polysilanes **1**–**3** are obtained as pale-yellow viscous gums in 48–60% isolable yield. These are soluble in common organic solvents such as toluene, THF, hexane, chloroform, dichloromethane, benzene etc. GPC data of **1**–**3** show a monomodel molecular weight distribution with $M_w$ ranging between 3100 and 5200 and polydispersity 1.1–2.1. In accord with the earlier trends [2e,14], the formation of **1** proceeds with the selective dehydrocoupling at primary SiH site only. $^1$H-NMR spectrum of each polymer shows broad unresolved signals in the regions characteristic of functional groups protons. While a broad resonance between $\delta$ 3.4–3.8 is attributed to the backbone SiH protons, polymer **1** shows a fortuitous chemical shift equivalence of the carbosilyl SiH protons in the same region. The integrated proton ratio of various groups is in accord with the idealized structure as shown in Scheme 1. In the $^{29}$Si{$^1$H}-NMR spectra, the silicon atoms associated with the carbosilyl groups appear in the region similar to that observed in the corresponding precursors, although the observed pattern is reminiscent of configurational sequence of the polymer chain (see below). DEPT$^{29}$Si-NMR spectra



Where $R^1$=H, R=Me (**1**);

$R^1$= R= Et (**2**);

$R^1$=Ph, R=Me (**3**)

Scheme 1.

allow the detection of backbone SiH and $SiH_2$ end groups at δ −51.0 to −61.5 and −48.5 to −53.2, respectively. There was no evidence of the presence of additional quaternary silicon centers that would be associated with polymer crosslinking. Further confirmation of the spectral assignments for **1** has been made on the basis of ($^{1}H$–$^{29}Si$) HSQC NMR spectrum which reveals two cross peaks at δ −7.3 to −10.8/3.7–3.9 and −51.2 to −61.5/3.5–3.8 (Fig. 1). Based on these results, the downfield chemical shift resonance at δ 3.7–3.9 is assigned to $Me_2SiH$– and upfield values (δ 3.5–3.8) to backbone SiH protons. DEPT-135 $^{13}C$-NMR spectra of **1**–**3** reveal distinct signals due to the different functional carbosilyl groups and are accordingly assigned.

Thermogravimetric analysis (TGA) of **1**–**3** shows different thermal stability behavior (30–800 °C, nitrogen atmosphere) (Fig. 2). For **1**, a gradual weight loss is observed up to 650 °C yielding 74% residual yield while the polymers **2** and **3** show two successive thermal decomposition steps at temperature ranging between 110–220 and 350–580 °C. The residual yields obtained in these samples (45% for **2**; 48% for **3**) are much lower than that observed for **1**. Although detailed pyrolysis studies are warranted, high residual yield in **1** may be attributed to thermally induced Kumada-type rearrangement [2] and/or cross-linking at the carbosilyl functional groups. Also, trace amount of titanium catalyst if present in the polymers can be reactivated thermally [2e] and result in high ceramic yields.

### 2.3. Microstructure of polysilanes

In principle, the polysilanes **1**–**3** may adopt isotactic (all *meso*), syndiotactic (all racemic) or atactic (random) configuration [16]. An examination of $^{29}Si$-NMR spectra of these polysilanes indicate a broad and complex pattern of signals due to the backbone. This is not surprising since the $^{29}Si$-NMR spectra of previously known polysilanes derived from dehydrocoupling of prochiral monomers invariably exhibit similar trends

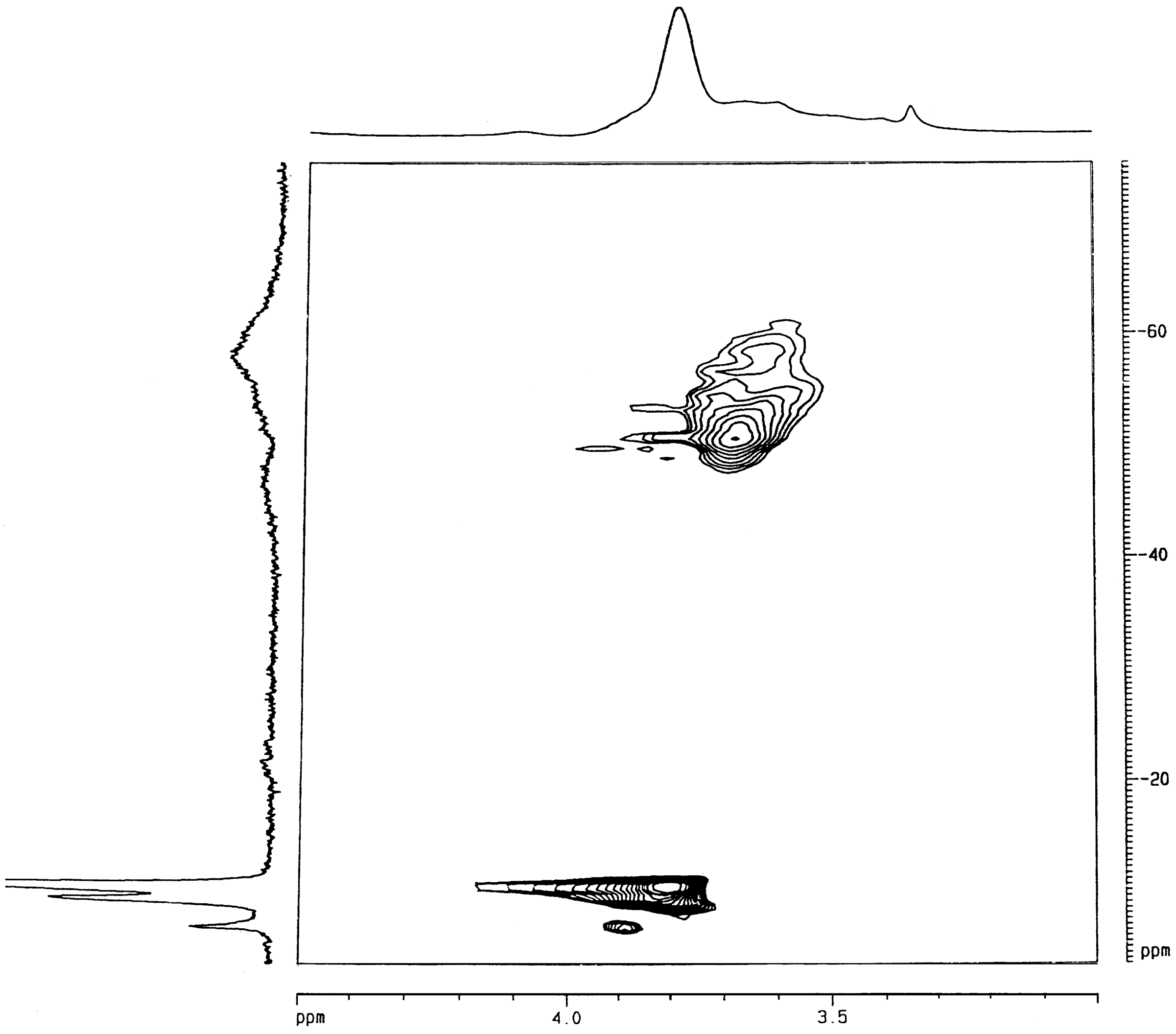


Fig. 1. ($^{1}H$–$^{29}Si$) HSQC NMR spectrum of polysilane **1**.

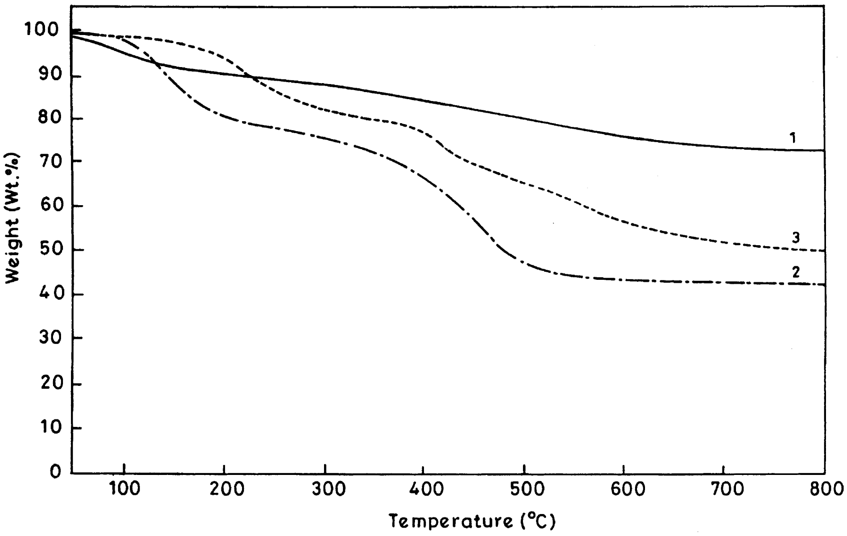


Fig. 2. Thermogravimetric analysis (TGA) of polysilanes **1**–**3**.

due to the presence of adjacent stereogenic silicon centers [8]. On the other hand, the signals associated with the dangling carbosilyl side chains in **1**–**3** are quite distinct and well resolved. With the assumption that the spectral pattern of the side chain is reminiscent of configurational sequences as reported recently for poly(*p*-tolylsilane) [8k], an attempt has been made to use carbosilyl group as a NMR probe for polymer tacticity.

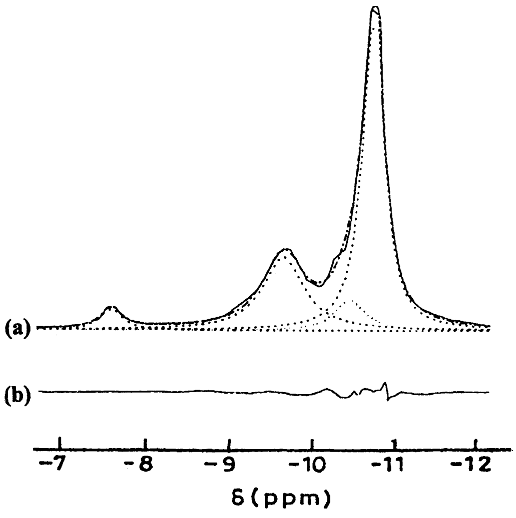


Fig. 3. (a) Partial $^{29}$Si-NMR spectrum of **1** depicting carbosilyl region; — spectrum, -.-.- calculated spectrum; .... deconvoluted peaks. (b) Difference spectrum of the actual and calculated spectrum.

$^{29}$Si-NMR spectrum of **1** shows three distinct signals at $\delta$ −7.3, −9.7 and −10.8 along with a minor signal at −10.2 associated with the carbosilyl–silicon atoms. The intensity of triad level stereodomains was evaluated by deconvolution of spectral region (Fig. 3). The fit between real and calculated spectra was sufficiently close and difference spectra of two matched within 1.0% error. By analogy with the literature trends [6b,8b,8h] the low field signals at $\delta$ −7.3 and −9.7 are tentatively assigned to mm and mr/rm stereodomains, respectively, while the signals at $\delta$ −10.2 and −10.8 are included in the rr stereodomain. On the basis of deconvolution studies, the signal intensity of each chemical shift region was deduced and triad intensity ratio (mm:mr:rr) was observed as 0.04:0.28:0.68. The validity of the parent triad assignments has been examined in terms of Bernoullian statistical model [17]. Based on the intensity of the rr triad sequence, the Bernoullian model reveals probability of the *meso* stereoreplication ($P_m = 1 - P_r$) as 0.18 and an estimate of the predicted intensity ratio is observed as 0.03(mm):0.29(mr):0.68(rr). Significantly, these values are in excellent agreement with those obtained from the deconvoluted spectrum. The probability of racemic replication ($P_r$) is observed as 0.82. Similarly for polysilane **2**, the $^{29}$Si-NMR spectrum comprising of five peaks in the region $\delta$ 7.0 to 9.4 due to dangling side chain was analyzed by deconvolution techniques. Fig. 4 shows the $^{29}$Si-NMR spectrum (carbosilyl region), the calculated spectrum and the difference map between the two which converged within 1.0% error. During the optimization of deconvoluted spectrum, the signals at $\delta$ 7.0–7.8 and 8.3–8.6 are assigned to rr and mr/rm triad sequences, respectively, while the resonance at $\delta$ 9.4 to mm stereodomain. Table 1 summarizes the relevant data pertaining to the triad level concentration of the parent peaks (from the $^{29}$Si-NMR spectrum) and those calculated on the basis of Bernoullian statistical model. An excellent agreement between these values is observed in this case too. Using the similar deconvolution method, the relative intensities for the triad resonances (mm:rm/mr:rr) in polysilane **3** was observed as 0.09: 0.14: 0.77. The data, however, fails to suitably match the Bernoul-

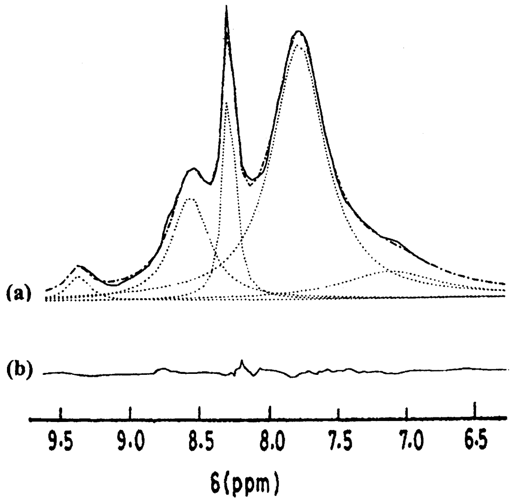


Fig. 4. Partial $^{29}$Si-NMR spectrum of **1** depicting carbosilyl region; — spectrum, -.-.- calculated spectrum; ….. deconvoluted peaks. (b) Difference spectrum of the actual and calculated spectrum.

lian statistical model presumably due to the overlapping of signals associated with these triad domains.

If the assumptions of the chemical shift regime of different triad sequence is correct, the data obtained herein for **1** and **2** gives appreciably high values of racemic enchainment probability, $P_r$ (0.82 for **1**; 0.84 for **2**). The number average sequence length for respective *meso* and racemic addition [17] i.e. $n_m$ and $n_r$ are found to be 1.28, 5.86 for **1**, and 1.15, 6.18 for **2**, which indicates that average chain length for racemic addition is more than for *meso* addition in the polysilanes. Thus on the basis of above data a syndiotactic rich configuration is expected. It is, however, imperative to mention that the interchange in the $\delta$ $^{29}$Si assignments of rr and mm configurations will not effect the Bernoullian statistics but will result in isotactic preference of the configuration. Given the choice between these extremes, syndiotactic arrangement seems more plausible on the basis of steric arguments and is in agreement with previous results on related configurational studies [6b,8b,8h].

These results are in contrast to the previously known microstructure of poly(phenylsilane) and poly($p$-tolylsilane) prepared from catalytic dehydropolymerization method [8g,8h,8j,8k]. In these polymers, Bernoullian statistical arguments reveal predominantly atactic configuration with marginal bias towards syndiotactic character. On the other hand, available data on the tacticity of poly(alkylsilane)s formed by the catalytic approach is quite limited. Corey et al. [18] have reported the formation of $H[BuSiH]_4H$ in which the formation of one stereoisomer is strongly favored suggesting a stereoselective chain growth. It thus appears that the microstructure of polymers **1** and **2** may find an analogy with that of $H[BuSiH]_4H$. Recently the results obtained on the microstructure analysis of polysilanes have been implicated to throw light on the mechanism of the chain growth during the catalytic process. Among the various factors, the stereochemical outcome is believed to arise from the interaction of chain end substituents $RPSiH_2$ (P = Polymer) with the metal center during Si–Si bond forming transition state [8g,8j]. The results obtained herein and also those reported earlier [18] suggest that the substituent effect (alkyl vs. aryl) of the primary silane precursors may also influence the tacticity of resulting polymers.

In conclusion, the polysilanes **1**–**3** bearing the carbosilyl side chain have been synthesized by titanium catalyzed dehydrocoupling and serve as representative models to probe the polymer tacticity using the side chain silicon atoms as the NMR probe. The microstructure analysis is based on deconvolution of $^{29}$Si-NMR signals of the carbosilyl groups and delineating the triad concentration ratios therefrom. While the results for **1** and **2** are in good agreement with the Bernoullian statistical model, that of **3** does not follow similar statistics. Determination of the microstructure of these polymers using $^{29}$Si-NMR studies of side chain silicon atoms finds a close analogy with a seminal report on the poly($p$-tolylsilane) in which the $^1$H-NMR spectrum of the side chain substituent (methyl group) is used to deduce microstructure [8k]. Although a syndiotactic rich configuration is predicted for these polysilanes, the validity of this method needs to be strengthened by correlating these data with those obtained from $^{29}$Si-NMR analysis of the polymer backbone.

Table 1
Experimentally and statistically determined triad concentration ratio for **1** and **2**

| Polymers | Triads | Experimentally found unit ratio | Statistical calculated unit ratio | $P_m$ | $P_r$ |
|---|---|---|---|---|---|
| **1** | rr | 0.68 | 0.68 | | |
| | mr/rm | 0.28 | 0.29 | | |
| | mm | 0.04 | 0.03 | 0.18 | 0.82 |
| **2** | rr | 0.70 | 0.70 | | |
| | mr/rm | 0.27 | 0.27 | | |
| | mm | 0.02 | 0.03 | 0.16 | 0.84 |

## 3. Experimental

### 3.1. General comments

All operations were carried out using standard Schlenk line techniques under dry nitrogen atmosphere. Solvents were freshly distilled under inert atmosphere over sodium benzophenone ketyl (diethylether) or phosphorous pentoxide (*n*-hexane) before use. Trichlorovinylsilane and chlorodimethylsilane (Aldrich) were distilled over Mg prior to use. Triethylsilane, dimethylphenylsilane, Karstedt's catalyst, lithium aluminium hydride, $Cp_2TiCl_2$ and *n*-butyl lithium (Aldrich) were used as received. The molarity of hexane solution of *n*-BuLi was confirmed by a titration method [19].

Infrared spectra were routinely obtained as thin films on a Nicolet FT-IR 460 (Protégé) spectrometer. $^{1}H$, $^{13}C$ and $^{29}Si$-NMR spectra were recorded in $CDCl_3$ on a Bruker 300DPX spectrometer at frequency of 300, 75.5 and 59.6 MHz, respectively. $^{13}C$ and $^{29}Si$-NMR spectra in DEPT mode were obtained using standard pulse sequence with a *J* modulation time 3.7 ms and 2 s delay time. $^{1}H-^{29}Si$ (HSQC) spectra was recorded using standard pulse sequence with a relaxation delay of 2 s for each of the 512$t_1$ experiments [20]. The chemical shifts are quoted with respect to TMS. Peak deconvolutions were achieved using ORIGIN 6.0 software with a peak-fitting package for windows. Gel permeation chromatography of the polysilanes were carried out in THF solutions on a Waters associated liquid chromatograph comprising Ultrastyragel permeation columns, a 501 HPLC solvent delivery system and R-400 refractive index detector. TGA was carried out under nitrogen atmosphere (30–800 °C, heating rate 10 °C $min^{-1}$) on Perkin–Elmer, TGA-7, thermogravimetric analyzer.

### 3.2. Preparation of $Me_2HSiCH_2CH_2SiH_3$ (**1a**)

To a stirred solution of trichlorovinylsilane (10.6 g, 8.3 ml, 65.6 mmol) containing catalytic amount of Karstedt's catalyst ($10^{-5}$ mole of Pt/mole of silane used), chlorodimethylsilane (5.9 g, 7.0 ml, 63.0 mmol) was added dropwise. Induction period was observed after a 10–15 min resulting in an exothermic reaction. The temperature was maintained below 45 °C during this period. After the complete addition, the reaction mixture was heated to 40 °C for 6 h. The crude mixture was fractionally distilled (b.p. 85–88 °C/5 mmHg, yield 95%). The resulting chlorocarbosilane (15.2 g, 59.3 mmol) in diethylether was added dropwise to a dispersion of $LiAlH_4$ (4.7 g, 124.7 mmol) in ether at 0 °C. The contents were gently refluxed for 5–6 h and then hydrolyzed with 1 N HCl. Ether layer was extracted and dried over anhydrous $Na_2SO_4$. Thereafter, the solvent was removed and the contents were distilled under vacuum to yield **1a** as colorless liquid (b.p. 72–75 °C, yield 81%).$^{1}H$-NMR ($CDCl_3$):$\delta$ 0.09 (d, $^{3}J_{HH} =$ 3.78 Hz, $SiMe_2$); 0.64–0.78 (m, $-CH_2CH_2-$); 3.55 (t, $^{3}J_{HH} = 3.39$ Hz, $SiH_3$); 3.86–3.89 (m, Si*H*); $^{13}C$-NMR ($CDCl_3$): $\delta$ −4.4 ($SiMe_2$); −0.2 ($-CH_2SiH_3$); 10.4 ($SiHCH_2$); $^{29}Si$-NMR ($CDCl_3$): $\delta$ −10.7 (SiH); −54.5 ($SiH_3$); IR ($cm^{-1}$): 2149 ($\nu$SiH); 929 ($\delta$ $SiH_2$).

### 3.3. Preparation of $Et_3SiCH_2CH_2SiH_3$ (**2a**)

The reaction between triethylsilane (4.3 g; 6.0 ml; 37.5 mmol) and vinyltrichlorosilane (6.1 g, 4.8 ml; 37.7 mmol) was carried out following the procedure described for **1a**. The contents were heated for 70 °C for 5 h and distilled (b.p. 92–95 °C/5 mmHg, yield 88%). The distillate (9.2 g, 33.1 mmol) was treated with $LiAlH_4$ (2.0 g, 52.9 mmol) in diethylether. Subsequent work up gave **2a** as a colorless liquid (b.p. 50–52 °C/5 mmHg, yield 78%). $^{1}H$-NMR ($CDCl_3$): $\delta$ 0.51–0.76 (m, $CH_2SiH_3 +$ $CH_2$(Et)); 0.86–0.98 (m, $Et_3SiCH_2 + CH_3$(Et)); 3.53 (t, $^{3}J_{HH} = 3.61$ Hz, $SiH_3$); $^{13}C$-NMR ($CDCl_3$): $\delta$ 3.2 ($CH_2SiH_3$), 3.3 ($CH_3-CH_2Si-$), 7.6 ($Et_3SiCH_2-$), 7.7 ($CH_3$); $^{29}Si$-NMR ($CDCl_3$): $\delta$ 8.3 ($Et_3Si$); −54.1 ($SiH_3$); IR ($cm^{-1}$): 2144 ($\nu$SiH); 925 ($\delta$ $SiH_2$).

### 3.4. Preparation of $Me_2PhSiCH_2CH_2SiH_3$ (**3a**)

The reaction was carried out in a manner similar to that described for **1a** using dimethylphenylsilane (7.0 g; 8.0 ml; 52.1 mmol) and vinyltrichlorosilane (8.5 g, 6.7 ml, 52.6 mmol). The contents were heated at 75 °C for 6 h and distilled (b.p. 113–115 °C/5 mmHg, yield 79.5%). The chlorocarbosilane (12.4 g, 41.6 mmol) thus obtained was treated with $LiAlH_4$ (2.53 g, 66.6 mmol) to afford the product as a colorless liquid (b.p. 77–79 °C/5 mmHg, yield 70.8%). $^{1}H$-NMR ($CDCl_3$):$\delta$ 0.31 (s, $SiMe_2$); 0.67–76 (m, $CH_2SiH_3$); 0.80–0.87(m, $Me_2PhSiCH_2$); 3.55 (t, $^{3}J_{HH} = 3.71$Hz, $SiH_3$); 7.38–7.56 (m, Ph) $^{13}C$-NMR ($CDCl_3$): $\delta$ −2.9 ($SiMe_2$); −0.3 ($-CH_2SiH_3$); 12.2 ($SiHCH_2$); 128.3, 129.5, 134.1 (Si–Ph); $^{29}Si$-NMR ($CDCl_3$): $\delta$ −1.3 (SiH); −53.0 ($SiH_3$); IR ($cm^{-1}$): 2145 ($\nu$SiH); 926 ($\delta$ $SiH_2$).

#### 3.4.1. Polymerization reaction

In a typical procedure, the carbosilane **1a** (2.0 g; 16.9 mmol) was charged with $Cp_2TiCl_2$ (0.11 g; 0.44 mmol) and *n*-BuLi (0.60 ml, 1.60 M in hexane) under dry $N_2$ conditions. The solution immediately turned blue in color. The reaction mixture was heated at 50 °C for 48 h. Thereafter, *n*-hexane (40 ml) was added and dry air was bubbled in the solution until the intense color disappeared. The solid residue was filtered through a short column of celite and clear filtrate was kept under vacuum for several hours to remove the volatile materials. The resulting gummy residue was dissolved in minimum amount of pentane and methanol was added dropwise until the polysilane was obtained in a separate layer as oily viscous gum. The dissolution/separation procedure was repeated three times to remove the catalyst and decomposition products, yielding the polysilane **1** (Yield 58%). Following the similar procedure as above, the polymer **2** and **3** were obtained 48 and 60% yield, respectively.

For **1**: $^{1}$H-NMR (CDCl$_3$):$\delta$ 0.04 (s, SiMe$_2$); 0.54–0.98 (m, CH$_2$CH$_2$); 3.4–3.8 (SiH backbone+SiH$_2$ side groups); 3.7–3.9 (SiH pendant); $^{13}$C-NMR (CDCl$_3$): $\delta$ $-4.4$ (SiMe$_2$); 2.6–5.4 (–CH$_2$); 11.2–14.3 (Me$_2$-SiH$\mathit{CH_2}$); $^{29}$Si-NMR (CDCl$_3$): $\delta$ $-7.3$ to $-10.9$ (Me$_2$-SiH); $-51.3$ to $-61.5$ (SiH backbone+SiH$_2$ end groups); IR (cm$^{-1}$): 2108 ($\nu$SiH); UV (DCM, nm) 265; GPC (THF): $M_w = 5170$; $M_n = 2460$.

For **2**: $^{1}$H-NMR (CDCl$_3$): $\delta$ 0.34–1.18 (alkyl); 3.46–3.72 (SiH backbone+SiH$_2$ side groups); $^{13}$C-NMR (CDCl$_3$): $\delta$ 1.4–3.4 (CH$_3$–$\mathit{CH_2}$Si–+$\mathit{CH_2}$SiH), 6.4–8.4 (Et$_3$Si$\mathit{CH_2}$– +CH$_3$); $^{29}$Si-NMR (CDCl$_3$): $\delta$ 7.8, 8.3, 8.6, 9.4 (Et$_3$Si); $-51.6$ to $-60.7$ (SiH backbone+SiH$_2$ end groups); IR (cm$^{-1}$): 2117 ($\nu$SiH); UV (DCM, nm) 262; GPC (THF): $M_w = 4670$; $M_n = 3800$.

For **3**: $^{1}$H-NMR (CDCl$_3$):$\delta$ 0.38 (SiMe$_2$); 0.72–1.21 (–CH$_2$CH$_2$–); 3.46–3.78 ( SiH back bone+SiH$_2$ end groups); 7.47–7.61 (m, Ph) $^{13}$C-NMR (CDCl$_3$): $\delta$ $-3.1$ (SiMe$_2$); $-0.8$ to 3.7 (CH$_2$); 10.9 to 13.6 (PhMe$_2$-SiH$\mathit{CH_2}$); 128.7 to 134.9 (Si–Ph); $^{29}$Si-NMR (CDCl$_3$): $\delta$ 0.5 to $-1.9$ (SiH pendant); $-48.5$ to $-60.2$ (SiH backbone+SiH$_2$ end groups); IR (cm$^{-1}$): 2103 ($\nu$SiH); UV (DCM, nm) 261; GPC (THF): $M_w = 3110$; $M_n = 2880$.

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[17] Following equations are used in Bernoullian statistical model: $P_m + P_r = 1$; $mm = P_m^2$; $rr = (1 - Pm)^2$; $mr/rm = 2P_m(1 - P_m)$; $n_m = mm + 0.5\ mr/0.5\ mr$; $n_r = rr + 0.5\ mr/0.5\ mr$. Where $P_m$, $P_r$ and $n_m$, $n_r$ are the probability and number average sequence length of *meso* and racemic addition, respectively.

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