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Synthesis of poly(hydrosilane)s, $-[R^{1}(H)Si]_{n} - (R^{1} = (CH_{2})_{3}SiRR'_{2};$ R, R' = Me, Et or Ph) and their reactivity studies towards allyl/vinylsilanes

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Abstract

New poly(hydrosilane)s, $-[RR'_2Si(CH_2)_3SiH]_n - (R = R' = Et (1a); R = Ph, R' = Me (2a); R = Me, R' = Ph (3a))$ have been synthesized by catalytic dehydrocoupling of the corresponding carbosilane monomers 1–3 using Cp₂TiCl₂/2.2BuLi as the catalyst. Hydrosilylation reaction of 1a or 2a with allyltrimethyl/triethoxyvinyl/trichlorovinylsilane in the presence of AIBN as free radical catalyst affords the polysilanes 1b–d and 2b–d, respectively, bearing Si–Me/Si–OEt/Si–H functional groups appended on the carbosilyl side chain. UV absorption spectra of 1a–3a reveal a shoulder like absorption without any peak at 250–260 nm while the polysilanes 1b–d and 2b–d exhibit a distinct absorption with λ_{max} 274–299 nm and ε : 671–887 (Si repeat unit)⁻¹ dm³ cm⁻¹. A discernable bathochromic shift in the λ_{max} value is invariably observed in the polysilanes bearing appended SiMe₃ or Si(OEt)₃ group in comparison to that observed for the polysilanes bearing sterically less bulky SiH₃ group incorporated on carbosilyl side chain. The polysilanes, 4b–d derived from chemical modification of poly(phenylsilane) also exhibit similar spectral behavior (λ_{max} 314–328 nm; $\varepsilon = 1500-2700$ (Si repeat unit)⁻¹ dm³ cm⁻¹). These changes indicate that electronic properties of these polysilanes are sensitive to nature of pendant substituents on silicon backbone. © 2006 Elsevier B.V. All rights reserved.

Keywords: Carbosilanes; Dehydrocoupling; Poly(hydrosilane)s; Chemical modification

1. Introduction

Following the pioneering work of Harrod et al. [1], the reaction involving chemical transformation of primary organosilanes, $RSiH_3$ (alkyl or aryl) to linear polysilanes, $-[RSiH]_n$ using Group 4 metallocene catalysts has been actively pursued in a number of research groups [2]. This synthetic approach is unique in providing a direct access to low molecular weight polysilanes bearing SiH groups which can not be synthesized by classical Wurtz coupling method due to harsh reaction conditions. Considerable attention has been devoted to understand several factors such as nature of the metal catalyst, organosilane precur-

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sor, reaction conditions etc. in order to improve the yield and molecular weight of these linear polymers [3].

Chemical transformation of Si–H groups in poly(phenylsilane), –[PhSiH]_n– using a variety of reagents is well documented [4]. The polysilane is known to undergo hydrosilylation reaction with aldehydes, ketones or functional olefins in presence of AIBN as free radical catalyst to afford new polysilanes with pendant alkoxy groups or side chain alkyl substituents appended with hydroxyl, amino or carboxylic acid [4a]. Dehydrohalogenation of Si–H groups in poly(phenylsilane) has been reported under mild conditions to generate reactive Si–X (X = Cl or Br) functionalities which can be subsequently transformed using nucleophilic reagents such as alcohols or mercaptans to afford hetero-atom substituted polysilanes [5]. Another example of chemical modification of poly(hydrosilane)s includes Rh-catalyzed carbenoid insertion into the Si–H bond [6].

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Scheme 1. Reagents: (i) $Cp_2TiCl_2 \cdot 2.2BuLi$; (ii) $CH_2 = CHCH_2SiMe_3/CH_2 = CHSi(OEt)_3/CH_2 = CHSiCl_3$; (iii) AIBN.

Although there has been numerous reports on the transition-metal mediated dehydrocoupling of primary aryl silanes, related studies on primary alkyl silanes are quite meager [1a-c,21,n,7]. This may partly be attributed to low reactivity of alkyl silanes towards dehydrocoupling and/ or their tendency to undergo autoxidation under aerobic conditions [8]. In addition, relatively high volatility of lower alkyl silanes limits their use as precursors. Within the framework of our research interest on functional polysilanes, we have recently reported that carbosilanes of the general formula, $R_2R'SiXSiH_3$ (X = CH₂CH₂; CH(CH₃); R = R' = Me, Et, Ph or H) are useful candidates which undergo efficient Ti-catalyzed dehydrocoupling at elevated temperature to afford polysilanes $-[R_2R'SiXSiH]_n$ bearing carbosilyl moieties as the pendant groups [7]. Our interest in this class of polysilanes stems from a desire to expand the scope of reaction chemistry on the appended silvl moieties in addition to the reactivity of the Si-H groups. In a related study, we also reported high molecular weight polysilanes $-[R_3Si(CH_2)_xSiR^1]_n - (R = Me, Et or Ph; R^1 = Me,$ Ph; x = 2 or 3) by Wurtz coupling method [9]. It has been observed that electronic properties of these polysilanes are influenced by the pendant sila-alkyl chain length as well as by steric effect of substituents on the appended silvl groups. In continuation of this work, we report herein the synthesis of new poly(hydrosilane)s, $-[R_2R'Si(CH_2)_3SiH]_n - (1a-3a)$, Scheme 1) which have been synthesized by Ti-catalyzed dehydrocoupling of appropriate carbosilane precursors. Subsequent chemical modification of these polysilanes by free radical hydrosilylation with allyl/vinyl silanes has allowed the formation of functional polysilanes bearing asymmetrically substituted side chain carbosilyl moieties (Scheme 1). A detailed analysis of UV spectral data of these polysilanes and its comparison with those of the precursor poly(hydrosilane)s (1a–3a) has allowed to delineate the steric influence of carbosilyl substituents on the electronic properties of these hitherto unknown polysilanes. The details are reported herein.

2. Results and discussion

2.1. Synthesis and characterization of carbosilane monomers, $RR'_{2}Si(CH_{2})_{3}SiH_{3}$

The carbosilanes, $RR'_2Si(CH_2)_3SiH_3$ (R = R' = Et (1); R = Ph, R' = Me (2); R = Me; $\overline{R'} = Ph$ (3)) have been synthesized in two steps. In the initial step, hydrosilylation [10] reaction between equimolar quantities of allyltrichlorosilane and an appropriate hydrosilane RR'SiH in presence of Karstedt's [11] catalyst proceeds regioselectively to afford the corresponding β -addition products, RR₂Si $(CH_2)_3SiCl_3$. Subsequent treatment of these compounds with LiAlH₄ results in the isolation of the desired carbosilanes 1-3 as colorless, distillable liquids. The presence of only one isomer in these carbosilanes is elucidated by HPLC and identified by IR, ¹H, ¹³C{¹H}, ²⁹Si NMR and EI-Mass spectroscopy. The primary SiH₃ group in these compounds gives rise to characteristic IR absorptions at 2149–2148 (vSiH) and 924–923 (δ SiH₂) cm⁻¹ and a distinct ²⁹Si NMR resonance at δ –56.46 to –63.97 (q, SiH_3 , ${}^1J_{Si-H} = 191.5-192.3$ Hz). In addition, each carbosilane exhibits a sharp ${}^{29}Si$ resonance in the characteristic chemical shift region ($\delta 6.40$ to -6.92) of the pendant RR'₂Si moiety. ¹H and ¹³C{¹H} NMR spectra are quite straightforward and corroborate well with the composition of these compounds. The mass spectra (EI) reveal $[M-H]^+$ ion in each case, while structurally important fragment ions are discernable from Si–C bond cleavage. The relevant spectral data are summarized in Section 3.

2.2. Polymerization of 1-3

Following the procedure known in literature [2n,2o], dehydrocondensation reaction of the carbosilane monomers 1–3 in presence of catalytic amount of Cp₂TiCl₂/2.2BuLi (50 °C, 48 h) results in a viscous mass in each case. The isolation of low molecular weight linear polysilanes $-[RR'_2Si(CH_2)_3SiH]_n$ –1a–3a (Scheme 1) from the crude mixture has been effected by repeated fractional precipitation with *n*-hexane/methanol mixture. These are obtained as pale yellow viscous gums and are soluble in common organic solvents such as dichloromethane, chloroform, hexane, toluene, THF, etc. The results obtained from thermogravimetric analysis reveal that these are stable up to



Fig. 1. GPC profile of polysilane: (a) 2a (solid line); (b) 2c (dotted line).

Table 1 ¹H, ¹³C{¹H}, ²⁹Si{¹H} NMR, and GPC data of polysilanes

250-320 °C. However, subsequent weight loss is observed in a continuous manner up to 500 °C leaving a residual vield of 22–28%. GPC data shows a monomodal molecular weight distribution in each case with $M_w = 2168 - 2309$ and PDI = 1.16 - 1.28. A representative GPC profile of polysilane 2a is shown in Fig. 1. These polysilanes have been characterized by IR, and multinuclei $({}^{1}H, {}^{13}C{}^{1}H)$, ²⁹Si{¹H}) NMR studies and the pertinent data are given in Table 1. By analogy with literature precedence [21], IR absorption (Fig. 2a) at 2095–2105 cm⁻¹ is attributed to Si-H groups of the silicon backbone. The absence of IR bands in the region $\sim 2070-2090 \text{ cm}^{-1}$ suggests that the polysilanes are devoid of cyclic species. It is noteworthy to mention that IR spectral characteristics remain identical upon ageing the polysilanes under inert conditions. However, polysilane 1a undergoes autooxidation upon exposure leading to some degree of siloxane formation. This is evident from the appearance of new bands at 1080 and 2156 cm⁻¹ characteristic of siloxane containing Si-H groups [8]. The polysilanes 2a and 3a bearing appended PhMe₂Si/Ph₂MeSi groups in the carbosilyl chain are relatively stable under these conditions, presumably due to steric interference of the bulky silvl-substituents. ¹H NMR spectrum of each polysilane shows broad and featureless signals associated with side chain methylene protons while resonances due to silyl-substituted methyl, ethyl or phenyl groups are well resolved. A similar spectral behavior is observed in the ${}^{13}C{}^{1}H$ NMR spectra as well, the terminal silvl substituents featuring relatively sharp resonances. The spectral behavior shows a close analogy with those of previously reported polysilanes bearing carbosilyl groups [9] as well as with poly(methyl-*n*-alkylsilane)s [12] prepared by Wurtz coupling method. Accordingly, the unresolved ¹H and ${}^{13}C{}^{1}H$ resonances of methylene groups in the polymers **1a–3a** may be attributed to short spin–spin relaxation time of these nuclei. The assignments of overlapping ${}^{1}H$ and ${}^{13}C{}^{1}H$ signals of methylene and ethyl groups in 1a are made from DEPT-135 ${}^{13}C{}^{1}H{}$ and HSQC (${}^{1}H{}^{-13}C{}$) NMR spectra (Fig. 3) which shows distinct cross peaks at δ 23.26–22.38/1.38 (β-CH₂), 15.96–15.52/0.64 (γ-CH₂)

Polysilane	δ ¹ H NMR (ppm)	$\delta^{13}C{^1H} NMR (ppm)$	δ^{29} Si{ ¹ H} NMR (ppm)	$M_{ m w}$	PDI	
1a	3.52 (br, Si <i>H</i> backbone), 1.38 (br,	23.26–22.38 (β- <i>C</i> H ₂), 15.96–	6.96 (Et ₃ <i>Si</i>) -57.18 to -65.43 (br, SiH	2309	1.17	
	2H, β-CH ₂), 0.85 (t, $J_{H-H} =$	15.52 (γ -CH ₂), 14.62–13.15	backbone)			
	7.8 HZ, CH_3 -Et + α - CH_2), 0.64	$(\alpha - CH_2), /.48 (CH_3 - Et),$				
	(br, 2H, γ -CH ₂), 0.56–0.48 (q,	$3.41 (CH_2-Et)$				
	6H, CH_2 -Et, $J_{H-H} = 7.8$ Hz)					
2a	7.49, 7.33 (br, 5H, Si <i>Ph</i>), 3.51 (br,	139.39, 133.52, 128.80, 127.73	-2.63 (PhMe ₂ Si) -57.30 to -65.15 (br,	2168	1.28	
	Si <i>H</i> backbone), 1.44 (br, 2H,	(Si– <i>Ph</i>), 23.52–22.42 (β- <i>C</i> H ₂),	SiH backbone)			
	β -CH ₂), 0.81 (br, 4H, α - and	20.50–19.65 (γ-CH ₂), 14.81–13.52				
	γ -CH ₂), 0.26 (br, 6H, PhMe ₂ Si)	$(\alpha - CH_2), -2.90 (PhMe_2Si)$				
3a	7.54, 7.28 (br, 10H, SiPh), 3.37	139.43, 134.12, 129.53, 128.87	-7.02 (Ph ₂ MeSi) -57.02 to -65.70 (br,	2264	1.16	
	(br, Si <i>H</i> backbone), 1.42 (br, 2H,	(Si-Ph), 23.45-22.03 (β-CH ₂),	SiH backbone)			
	β -CH ₂), 0.81 (br, 2H, α -CH ₂),	20.26–19.97 (γ-CH ₂), 14.63–13.79	,			
	0.64 (br, 2H, γ -CH ₂), 0.48 (br,	$(\alpha - CH_2), -3.84 (Ph_2Me_2Si)$				
	3H, Ph ₂ MeSi)					



Fig. 2. IR spectra of: (a) 1a; (b) hydrosilylated product of 1a with vinyltrichlorosilane; (c) 1d.

and δ 7.48 (CH₃-Et), 14.62–13.15 (α -CH₂)/0.85. ²⁹Si{¹H} NMR spectra invariably show a singlet at δ 6.96 to -7.02 and a broad featureless signal at δ -57.30 to -65.70 which are attributed to the carbosilyl side groups and to silicon backbone, respectively.

2.3. Chemical modification

The Si–H groups in polysilanes **1a** and **2a** have been subjected to free radical hydrosilylation reaction with allyltrimethyl/triethoxyvinyl/trichlorovinylsilane (toluene, 80– 90 °C) in presence of AIBN as the catalyst. The extent of hydrosilylation was monitored at different time intervals by IR (Fig. 2b) and ¹H NMR spectroscopy. The concentration of Si–H content in the reaction mixture was found to decrease with time and finally remains practically unchanged after 48 h. The isolation of the corresponding polysilanes **1b–d** and **2b–d** (Scheme 1) has been achieved by fractional precipitation of the crude product using THF/methanol mixture.



The polysilanes, thus obtained are pale yellow viscous gums and are soluble in common organic solvents such as dichloromethane, chloroform, hexane, toluene, THF, etc. The results of thermogravimetric analysis reveal that these are stable up to 300–350 °C. However, a continuous weight loss is observed up to 500 °C leaving a residual yield of 23-36%. These polysilanes show a monomodal molecular weight distribution in each case with $M_{\rm w} = 2289-4780$; PDI = 1.25 - 1.78. A GPC profile of a representative polysilane 2c along with the parent poly(hydrosilane) 2a is shown in Fig. 1 for comparison and the relevant data are given in Table 2. These results apparently suggest that free radical hydrosilvlation of the parent poly(hydrosilane)s occurs without scission of the silicon backbone. However, a perceptible reduction of molecular weight for 1d and 2d in comparison to those of the corresponding poly(hydrosilane)s may be attributed to arise during the step involving reduction of Si-Cl groups with lithium aluminium hydride [5a]. IR spectra of the polysilanes reveal a very weak absorption at 2092–2101 cm⁻¹ (except for **1d** and **2d**) due to residual Si-H group of the backbone. Characteristic absorptions for the functional groups associated with carbosilyl chain appear at 1250-1246 (Si-Me), 1080-1079, (Si–OEt) and 2147–2145 (vSiH₃); 922–921 (δ SiH₃) cm⁻¹ (Fig. 2c). These results coupled with ¹H NMR spectral data suggest that the chemical transformation of poly(hydrosilane)s under these conditions occurs with >90% inclusion of the carbosilyl moiety. ¹H and ¹³C{¹H} NMR spectra show broad and overlapping signals due to methylene and/or ethyl (for 1b-d only) groups associated with the carbosilyl moiety. The overlapping ${}^{1}H$ and ${}^{13}C{}^{1}H$ resonances of methylene groups has been assigned from HSQC

Table 2

¹H, ¹³C{¹H}, ²⁹Si{¹H}/²⁹Si NMR, UV and GPC data of polysilanes

Polysilane	δ ¹ H NMR (ppm)	$\delta^{13}C{^1H} NMR (ppm)$	δ^{29} Si{ ¹ H}/ ²⁹ Si NMR	UV ^a $\lambda_{max}/\varepsilon$	$M_{ m w}{}^{ m b}$	PDI ^c
			(ppm)			
1b	1.44 (br, β-/β'-CH ₂), 0.94 (t, ³ J _{H-H} = 7.6 Hz, CH ₃ -Et + α-/α'- CH ₂), 0.62 (br, γ-/γ'-CH ₂), 0.51 (br, CH ₂ -Et), 0.00 (br, SiMe)	22.47 (γ' -CH ₂), 21.88 (β -CH ₂), 20.15 (α -CH ₂), 17.64 (α' -/ β' - CH ₂), 16.61 (γ -CH ₂), 7.54 (CH ₃ - Et), 3.46 (CH ₂ -Et), -1.52 (Si-	6.02 (Et_3Si), 0.00 ($SiMe_3$) -30.03 (br, Si backbone)	296/671	4780	1.78
1c	3.72 (br, CH_2 -OEt), 1.36 (br, β - C H_2), 1.13 (br, CH_3 -OEt), 0.85 (br, CH_3 -Et + α/α' -C H_2), 0.54, 0.44 (γ -/ β' -C H_2 + C H_2 -Et)	<i>Me</i> ₃) 58.86 (CH ₂ –OEt), 21.46 (β-CH ₂), 20.38 (α-CH ₂), 19.05 (CH ₃ –OEt), 17.56 (γ-CH ₂), 7.89 (CH ₃ –Et), 6.97, 5.42 (α'-/β'-CH ₂), 3.12 (CH ₂ –Et)	5.93 (Et ₃ <i>Si</i>), -29.89 (br, Si backbone), -46.25 (<i>Si</i> -(OEt) ₃)	293/732	3310	1.36
1d	3.49 (br, SiH ₃), 1.32 (br, β-CH ₂), 0.86 (t, ${}^{3}J_{H-H} = 7.6$ Hz, CH ₃ – Et + α-CH ₂), 0.67 (br, α'-/β'- CH ₂), 0.55 (br, γ-CH ₂), 0.44 (br, CH ₂ -Et)	21.83 (β -CH ₂), 19.39 (α -CH ₂), 17.20 (γ -CH ₂), 9.56 (α '-CH ₂), 7.53 (CH ₃ -Et), 3.44 (CH ₂ -Et), 1.02 (β '-CH ₂)	6.86 (Et ₃ <i>Si</i>), -30.55 (br, Si backbone), -48.03 , -51.28, -54.52 , $-57.76(q, SiH3, 1JSi-H =193.1 Hz)$	278/824	2394	1.41
2b	7.50, 7.28 (br, Si– <i>Ph</i>), 1.42 (br, β -/ β '-C <i>H</i> ₂), 0.84 (br, α -/ α '/ γ - C <i>H</i> ₂), 0.57 (γ '-C <i>H</i> ₂), 0.28 (br, Ph <i>Me</i> ₂ Si), 0.00 (br, Si <i>Me</i> ₃)	139.42, 133.44, 128.76, 127.73 (Si– <i>Ph</i>), 22.35 (γ'-CH ₂), 21.83 (β-CH ₂), 20.17 (γ-/ α -CH ₂), 17.68 (α' -/ β' -CH ₂), -1.41 (Si– <i>Me</i> ₃), -2.81 (Ph <i>Me</i> ₂ Si)	1.26 (<i>Si</i> Me ₃)-3.10 (PhMe ₂ <i>Si</i>)-30.78 (br, Si backbone)	299/822	2952	1.25
2c	7.44, 7.25 (br, Si– <i>Ph</i>), 3.73 (br, C <i>H</i> ₂ –OEt), 1.42 (br, β -C <i>H</i> ₂), 1.15 (br, C <i>H</i> ₃ –OEt), 0.78 (br, α -/ γ -/ α' -/ β' -C <i>H</i> ₂), 0.21 (br, Ph <i>Me</i> ₂ Si)	139.39, 133.41, 128.72, 127.68 (Si– <i>Ph</i>), 58.21 (<i>C</i> H ₂ –OEt), 21.38 (β - <i>C</i> H ₂), 19.64 (γ - <i>C</i> H ₂), 18.40 (<i>C</i> H ₃ –OEt), 17.62 (α - <i>C</i> H ₂), 6.65, 4.50 (α '-/ β '- <i>C</i> H ₂), -2.94 (Ph <i>Me</i> ₂ Si)	-3.18 (PhMe ₂ Si) -27.23 (br, Si backbone), -45.35 (Si-(OEt) ₃)	296/887	3801	1.63
2d	7.50, 7.35 (Si– <i>Ph</i>), 3.54 (br, Si <i>H</i> ₃), 1.42 (br, β - <i>CH</i> ₂), 0.82 (br, α -/ γ -/ α '-/ β '- <i>CH</i> ₂), 0.27 (Ph <i>Me</i> ₂ Si)	139.24, 133.48, 128.80, 127.74 (Si– <i>Ph</i>), 20.30 (β -/ γ - <i>C</i> H ₂), 16.90 (α - <i>C</i> H ₂), 8.76 (α '- <i>C</i> H ₂), 2.54 (β '- <i>C</i> H ₂), -2.86 (Ph <i>Me</i> ₂ Si)	-3.15 (PhMe ₂ Si) -28.67 (br, Si backbone), -48.79, -52.02, -55.25, -58.48 (q, SiH ₃ , ¹ J _{Si-H} = 192.5 Hz)	274/873	2289	1.54
4b	7.18 (br, Si <i>Ph</i>), 1.10 (br, α' -/ β' -/ γ' -CH ₂), 0.00 (br, Si <i>Me</i>)	136.68, 134.23, 127.46 (Si– <i>Ph</i>), 21.83 (α' -/ β' -/ γ' - <i>C</i> H ₂), -1.64 (Si <i>Me</i> ₃)	0.78 (<i>Si</i> Me ₃) -32.46 (br, Si backbone)	328/2400	4002 (2628) ^d	1.52 (1.32) ^d
4c	7.00 (br, Si <i>Ph</i>), 3.46 (br, CH ₂ -OEt), 1.01 (br, α' -/ β' - CH ₂ + CH ₃ -OEt)	136.55, 134.16, 127.53 (Si– <i>Ph</i>), 58.06 (<i>C</i> H ₂ –OEt), 18.22 (<i>C</i> H ₃ – OEt), 5.42 (α' -/ β' - <i>C</i> H ₂)	-30.17 (br, Si backbone), -46.19 (<i>Si</i> -(OEt) ₃)	323/2700	7122 (3505) ^d	2.05 (1.38) ^d
4d	7.18 (br, Si <i>Ph</i>), 3.31 (br, Si H_3), 0.81 (br, α' -/ β' -C H_2)	136.39, 133.77, 127.89 (Si– <i>Ph</i>), 8.69 (α'- <i>C</i> H ₂), 1.84 (β'- <i>C</i> H ₂)	-32.01 (br, Si backbone), -48.51, -51.75, -54.99, -58.24 (q, SiH_3 , ${}^{1}J_{Si-H} =$ 193.1 Hz)	314/1500	2348 (3175) ^d	1.33 (1.46) ^d

^a ε units: (Si repeat unit)⁻¹ dm³ cm⁻¹; λ_{max} units: nm.

^b Molecular weights determined by GPC relative to polystyrene standards; eluant: THF; 25 °C.

^c PDI = polydispersity index (M_w/M_n) .

^d Molecular weight of poly (phenysilane) prepared under different runs.

(¹H–¹³C{¹H}) NMR spectrum of a representative polysilane **1b** (Fig. 4) which shows cross peaks at δ 21.88, 17.64/1.44 (β-/β'-CH₂), 16.61, 22.47/0.62 (γ-/γ'-CH₂), 20.15, 17.64, 7.54/0.94 (α-/α'-CH₂, CH₃–Et). A detailed assignment for other polysilanes has been made accordingly and pertinent spectral data are given in Table 2. ²⁹Si{¹H} NMR spectra reveal sharp resonances in the chemical shift region which are characteristic of appended silicon moieties. The ²⁹Si{¹H} resonances due to silicon backbone appear at δ –27.23 to –30.78 showing broad and featureless profile. For **1d** and **2d**, the presence of appended SiH₃ group is confirmed by ²⁹Si signal at δ –48.03 to –58.48 (quartet, ¹J_{Si-H} = 192.5–193.1).

In order to get an insight into the free radical hydrosilylation approach, poly(phenylsilane) was also subjected to chemical modification by AIBN catalyzed reaction with allyltrimethyl/triethoxyvinyl/trichlorovinylsilane. This has resulted in the isolation of linear polysilanes **4b–d** bearing phenyl and carbosilyl groups as pendant substituents. There is no evidence of Si–Si bond cleavage during hydrosilylation from the GPC data which shows a monomodal molecular weight distribution with $M_w = 2348-7122$ and PDI = 1.33-2.05. IR and ¹H NMR spectra of these polysilanes suggest the inclusion of 75–85% carbosilyl moiety as the pendant groups. The presence of residual Si–H groups in the polymeric framework is evident by a weak IR



Fig. 4. $(^{1}H-^{13}C)$ HSQC NMR spectrum of **1b**.

absorption at 2094–2103 cm⁻¹, while characteristic absorptions associated with the carbosilyl moieties appear at 1246 (SiMe), 1079 (Si–OEt) or 2143 (ν SiH₃); 924 (δ SiH₃) cm⁻¹. ¹H, ¹³C{¹H} and ²⁹Si{¹H} NMR spectra are consistent with the idealized composition of these polysilanes and the relevant data are summarized in Table 2. For 4d, ²⁹Si NMR spectrum reveals a quartet at δ –48.51 to –58.24 (¹J_{Si–H} = 193.1 Hz) due to the presence of appended SiH₃ group.

2.4. UV spectral studies

UV spectral studies of all the polysilanes have been performed to gain an insight into the electronic properties associated with σ delocalized silicon backbone. The relevant data are summarized in Table 2 while the spectral profiles of the polysilanes **1a-d** are shown in Fig. 5. For poly(hydrosilane)s 1a-3a, the spectra invariably show a shoulder like absorption without any peak at 250-260 nm. A detailed comparison of these results with those of previously known poly(hydrosilane)s, $-[RSiH]_n - (R = alkyl)$ is precluded due to lack of adequate information in the literature [1a,5b,13]. However, the observed UV spectral behavior is believed to arise as a result of predominantly gauche conformation of the silicon backbone due to size difference between hydrogen and the bulky carbosilyl pendant groups [4a]. Contrary to this, the modified polysilanes 1b-d and 2b-d derived from poly(hydrosilane)s 1a and 2a, respectively, exhibit a broad and distinct absorption with λ_{max} 274–299 nm and molar absorptivity (ε : 671–887 (Si repeat unit)⁻¹ dm³ cm⁻¹). The observed bathochromic shift in the λ_{max} values as compared to those of the precursors may be attributed to chain stiffen-



Fig. 5. UV spectra (cyclohexane, RT) of polysilanes 1a-d.

ing due to steric effect of long carbosilyl chain which impart more extended trans conformation to the silicon backbone. A scrutiny of the spectral profiles of the polysilanes 1b-d (Fig. 5) also reveal a significant dependence of the λ_{max} values on the nature of the appended sila-substituents on the side chain. A discernable bathochromic shift in the λ_{max} value is observed in the polysilanes **1b**-c bearing appended SiMe₃/Si(OEt)₃ group in comparison to that observed for the polysilanes 1d bearing sterically less bulky SiH₃ group. It is interestingly to note that UV spectra of the polysilanes **2b-d** also follow a similar trend. To comprehend these results, the polysilanes **4b–d** bearing phenyl and carbosilyl groups on the silicon backbone have also been studied with regard to their electronic properties. In accord with literature precedence [4a], poly(phenylsilane) obtained under different runs shows a weak absorption with λ_{max} at \sim 300 nm due to σ - σ ^{*} transition of the silicon backbone while the corresponding absorption for 4b-d are discernable at 314-328 nm with $\varepsilon = 1500-2700$ (Si repeat unit)⁻¹ dm³ cm⁻¹ (Fig. 6). Interestingly, the relative magnitude of the observed bathochromic shift in these polysilanes follows the order: $4d(314) \le 4b(328) \sim 4c(323)$ which correlates well with those of polysilanes 1b-d with similar sila-substituents on the carbosilyl group.

In conclusion, the poly(hydrosilane)s 1a-3a have been synthesized by titanium catalyzed dehydrocoupling of carbosilane monomers with terminal SiH₃ groups. These



Fig. 6. UV spectra (THF, RT) of polysilanes 4a-d.

polysilanes serve as models to probe the reactivity of Si-H groups towards allyl/vinylsilanes under free radical catalyzed conditions. Using this approach, a number of funcsubstituted polysilanes 1b-d tionally and 2b-d incorporating reactive Si-H or Si-OEt appended functional groups on the carbosilyl chain have been synthesized. It is noteworthy that these polysilanes are inaccessible via Wurtz coupling route. These results assume significance in view of lack of reported studies on the reactivity of poly(hydrosilane)s, $-[RSiH]_n$ (R = alkyl). These polysilanes show interesting variations in the electronic properties associated with σ - σ ^{*} transition. For 1a-3a, the appearance of shoulder like absorption at 250-260 nm in the UV spectra is suggestive of predominantly a gauche conformation of the silicon backbone. For polysilanes 1b-d and 2b-d derived from the precursor poly(hydrosilane)s, the observed spectral parameters [λ_{max} 274– 299 nm and ε : 671–887 (Si repeat unit)⁻¹ dm³ cm⁻¹] are indicative of chain stiffening and greater population of trans segments in the silicon backbone. In addition, the observed variation in the λ_{max} values correlates with the steric demand of appended sila-substituents, SiH₃, SiMe₃ and Si(OEt)₃. This is evident from the bathochromic shift of $\lambda_{\rm max}$ for the polysilanes bearing appended SiMe₃/ Si(OEt)₃ group in comparison to that observed for the polysilanes bearing sterically less bulky SiH₃ group on the carbosilyl side chain. These results are further corroborated from the UV spectral data of polysilanes 4b-d.

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 (ether, tetrahydrofuran, and toluene), phosphorus pentoxide (*n*-hexane), and magnesium (alcohols) before use. Glasswares were dried in an oven at 100-120 °C and further flame dried under vacuum prior to use. Allyltrichlorosilane and vinyltrichlorosilane (Aldrich) were freshly distilled over magnesium. Triethoxyvinylsilane and allyltrimethylsilane (Aldrich) were freshly distilled before use. Karstedt's catalyst (platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex), lithium aluminium hydride, butyl lithium (1.6 M in hexane), bis(cyclopentadienyl)titaniumdichloride, triethylsilane, phenyldimethylsilane and diphenylmethylsilane (Aldrich) were used as received. The molarity of hexane solution of n-BuLi was confirmed by titration method [14]. Poly(phenylsilane) was prepared by method known in literature [2n,2o]. AIBN [2,2'-azo(bisisobutyronitrile)] (Merck) was recrystallized from methanol before use.

Infrared spectra were obtained as thin films on KBr pellets on a Nicolet FT-IR (Protégé) spectrophotometer. EI-(70 eV) Mass spectra were carried out on VG analytical (Model 70-s) mass spectrometer. UV spectra were recorded on a Perkin-Elmer (Lambada Bio 20) spectrophotometer. Molecular weights of the polysilanes were estimated using Waters 510 liquid chromatograph equipped with a Varian 400 refractive index detector and Waters styragel HR3 and HR4 column in series. The chromatograph was calibrated with polystyrene standards and THF was used as eluent. HPLC data were obtained on Waters 1525 binary HPLC fitted with Waters dual wavelength absorbance detector and a C-18 column. n-Hexane was used as the mobile phase. ¹H, ¹³C and ²⁹Si NMR spectra were recorded in CDCl₃ on Bruker spectrospin DPX 300 MHz instrument at frequency 300, 75.5, 59.6 MHz, respectively, as well as ²⁹Si NMR spectra were also recorded on Bruker avance II 400 NMR spectrometer at frequency 79.49 MHz and chemical shifts are quoted relative to Me_4Si . ¹³C{¹H} spectra in DEPT-135 mode were obtained using standard pulse sequence with J modulation time 3.7 ms and 2 s delay time. HSQC $(^{1}H^{-13}C)$ spectra were recorded using standard pulse sequence with a relaxation delay of 2 s for each of 512t₁ experiments. Thermogravimetric analysis of polysilanes was carried out in N2 atmosphere between 50 and 800 °C at a heating rate of 10 °C/min on a Perkin-Elmer Thermal analysis system.

3.2. Synthesis of carbosilane precursors

The carbosilanes 1-3 were prepared by following the hydrosilylation approach. To a stirred solution of allyltrichlorosilane (8.61 g, 7.0 ml, 49.0 mmol) containing catalytic amount of Karstedt's catalyst (10⁻⁷ Pt/mol of silane), triethyl/phenyldimethyl/diphenylmethylsilane (48 mmol) was separately added dropwise at room temperature. The reaction mixture turned pale yellow after a few ml of hydrosilane was added. No induction period was observed during the complete addition. The reaction mixture was heated at 100 °C for 12 h in order to complete the reaction and the product obtained in each case was fractionally distilled. The resulting chlorocarbosilanes (40 mmol) were separately added dropwise to a dispersion of LiAlH₄ (2.43 g, 64.0 mmol) in the same solvent 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 Na₂SO₄. Thereafter the contents were distilled under vacuum to yield the corresponding carbosilane 1-3 as colorless liquids. The relevant spectroscopic data are given below. For assigning the NMR spectral data, methylene group attached to SiH₃ moiety is represented with the notation, (α -) and subsequent groups are designated with β - and γ -notations respectively.

3.2.1. $Et_3SiCH_2CH_2CH_2SiH_3$ (1)

(bp 48–50 °C/5 mm Hg, yield 60%). EI mass: 187 $[M-H]^+$, 159 $[M-CH_3CH_2]^+$, 115 $[Et_3Si]^+$, 87 $[Et_3]^+$. ¹H NMR: δ 3.47 (t, ³J_{H-H} = 3.7 Hz, 3H, SiH₃), 1.51–1.40 (m, 2H, β-CH₂), 0.92 (t, ³J_{H-H} = 7.9 Hz, 9H, CH₃–Et), 0.86–0.78 (m, 2H, α-CH₂), 0.63–0.58 (m, 2H, γ-CH₂), 0.54–0.46 (q, ³J_{H-H} = 7.9 Hz, 6H, CH₂–Et). ¹³C{¹H} DEPT-135

NMR: δ 21.29 (β-CH₂), 15.16 (γ-CH₂), 10.80 (αCH₂), 7.67 (CH₃-Et), 3.53 (CH₂-Et). ²⁹Si NMR: δ 6.40 (Et₃Si), -63.97, -61.55, -59.14, -56.73 (q, SiH₃, ¹J_{Si-H} = 191.5 Hz). IR (KBr, cm⁻¹) 2149 (νSiH), 924 (δSiH₂).

3.2.2. $PhMe_2SiCH_2CH_2CH_2SiH_3$ (2)

(bp 68–70 °C/5 mm Hg, yield 83%). EI mass: 207 $[M-H]^+$, 193 $[M-CH_3]^+$, 135 $[PhMe_2Si]^+$, 121 $[PhMe-SiH]^+$, 105 $[PhSi]^+$. ¹H NMR: δ 7.54–7.31 (m, 5H, Si*Ph*), 3.47 (t, ³J_{H-H} = 3.8 Hz, 3H, SiH₃), 1.56–1.45 (m, 2H, β-CH₂), 0.90–0.78 (m, 4H, α- and γ-CH₂), 0.27 (s, 6H, PhMe₂Si). ¹³C{¹H} DEPT-135 NMR: δ 134.30, 129.12, 128.83 (Si*Ph*), 21.56 (β-CH₂), 17.61 (γ-CH₂), 10.32 (α-CH₂), -3.67 (PhMe₂Si). ²⁹Si NMR: δ -3.42 (PhMe₂Si), -63.71, -61.30, -58.88, -56.46 (q, SiH₃, ¹J_{Si-H} = 192.3 Hz). IR (KBr, cm⁻¹) 2148 (vSiH), 924 (δ SiH₂).

3.2.3. $Ph_2MeSiCH_2CH_2CH_2SiH_3$ (3)

(bp 150–155 °C/5 mm Hg, yield 75%). EI mass: 269 $[M-H]^+$, 255 $[M-CH_3]^+$, 197 $[Ph_2MeSi]^+$, 105 $[PhSi]^+$. ¹H NMR: δ7.43–7.11 (m, 10H, SiPh), 3.36 (t, ³J_{H-H} = 3.6 Hz, 3H, SiH₃), 1.51–1.40 (m, 2H, β-CH₂), 1.10–1.04 (m, 2H, γ-CH₂), 0.77–0.74 (m, 2H, α-CH₂), 0.45 (s, 3H, Ph₂MeSi). ¹³C{¹H}NMR: δ 137.32, 134.62, 129.34, 128.02 (SiPh), 21.17 (β-CH₂), 17.84 (γ-CH₂), 10.49 (α-CH₂), -4.24 (Ph₂MeSi). ²⁹Si NMR: δ –6.92 (Ph₂MeSi), -63.80, -61.38, -58.96, -56.54 (q, SiH₃, ¹J_{Si-H} = 192.3 Hz). IR (KBr, cm⁻¹) 2148 (νSiH), 923 (δSiH₂).

3.3. Preparation of poly(hydrosilane)s 1a-3a

The carbosilane 1 (4.25 g, 22.5 mmol) was charged with Cp₂TiCl₂ (0.14 g, 0.56 mmol) and *n*-BuLi (0.77 mL, 1.6 M hexane) under dry N_2 conditions. The solution immediately turned blue in color. The reaction mixture was heated at 50 °C for 48 h and the catalyst was subsequently deactivated by adding *n*-hexane (30 mL) in air until the intense color disappeared. The solid residue was filtered and the filtrate was kept under vacuum for several hours to remove the volatile materials. The resulting gummy residue was dissolved in minimum amount of *n*-hexane and methanol was added drop wise until the polysilane was obtained in a separated layer as an oily viscous gum. The dissolution/ separation procedure was repeated three times to obtain the linear poly(hydrosilane)s 1a (2.38 g, Yield 57%). Following the similar procedure as above, the polysilanes 2a and 3a were obtained as gummy material using the monomers 2 and 3 respectively. Yield 64-73%.

3.3.1. Reactions of polysilanes **1a** and **2a** with allyltrimethyll triethoxyvinylsilane

The polysilane **1a** or **2a** (3.38 mmol) in toluene was subjected to free radical hydrosilylation with allyltrimethyl/triethoxyvinylsilane (5.60 mmol) in the presence of catalytic amount of AIBN (0.39 mmol). The contents were refluxed at 90 $^{\circ}$ C for 48 h. Thereafter, solvent was removed under vacuum leaving behind a viscous mass. The linear polysil-

anes **1b–c** and **2b–c** were separated from the corresponding crude products by repeated precipitation with THF/methanol mixture (yield = 34-41%).

3.3.2. Reactions of polysilanes **1a** and **2a** with trichlorovinylsilane

To a stirred solution of polysilane **1a** or **2a** (4.30 mmol) and AIBN (0.35 mmol) in toluene (5 mL) was added trichlorovinylsilane (7.86 mmol) and the solution was refluxed at 80 °C for 48 h. Excess of solvent was removed under vacuum. The resulting polysilane, (3.89 mmol) containing SiCl₃ terminal groups was dissolved in diethyl ether and was added to a dispersion of LiAlH₄ (6.0 mmol) in diethyl ether. The contents were gently refluxed for 4–5 h. The reaction mixture was hydrolyzed using 1 N HCl. Ether layer was separated and dried over anhydrous sodium sulphate. The linear polysilane **1d** and **2d** were separated from the corresponding crude mixture by repeated precipitation with THF/methanol mixture (yield 39–42%).

3.4. Reaction of poly(phenylsilane) with allyltrimethyll triethoxyvinylsilaneltrichlorovinylsilane

The reaction between poly(phenylsilane) (0.73 g, 6.88 mmol) and allyltrimethyl/triethoxyvinyl/trichlorovinylsilane (10.32 mmol) in presence of AIBN catalyst was performed under identical conditions as described above for similar hydrosilylation reactions of **1a** and **2a**. After usual workup, the corresponding polysilanes **4b–d** were obtained as pale yellow solids (yield 25–42%).

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