

Synthesis, characterization and UV spectral studies of copolysilanes, $\{[\text{RR}'_2\text{Si}(\text{CH}_2)_2\text{SiMe}]_x[\text{PhR}^1\text{Si}]_{1-x}\}_n$ ($\text{R}, \text{R}' = \text{Me}, \text{Et}$ or Ph ; $\text{R}^1 = \text{Me}$ or Ph) bearing carbosilyl side chains

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Abstract

A number of copolysilanes, $\{[\text{RR}'_2\text{Si}(\text{CH}_2)_2\text{SiMe}]_x[\text{PhR}^1\text{Si}]_{1-x}\}_n$ ($\text{R}, \text{R}' = \text{Me}, \text{Et}$ or Ph ; $\text{R}^1 = \text{Me}$ (**1–3**); Ph (**4–6**)) bearing carbosilyl side chains have been synthesized by Wurtz coupling method and characterized by GPC, multinuclear (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{29}\text{Si}\{^1\text{H}\}$) NMR and UV spectral studies. A detailed study of $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra suggests that the copolysilanes **1–3** are comprised of segregated runs of PhMeSi and RMeSi ($\text{R} = \text{carbosilyl}$) units while **4–6** possess many different configurational and conformational environments. The UV spectra of these copolymers reveal a distinct absorption (λ_{max}) at 312–352 nm due to $\sigma\text{--}\sigma^*$ transition and show a strong dependence on the polymer composition as well as nature of the appended sila substituents.

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1. Introduction

Polysilanes, $-\text{[RR}'\text{Si}]_n-$ ($\text{R} = \text{alkyl}$ or aryl) with linear catenated silicon backbone are interesting class of organo-silicon polymers owing to their electronic and optical properties associated with σ electron delocalization along the catenated silicon backbone [1]. This intrinsic property makes polysilanes potential candidates for applications in photoresist [2], microlithography [3], optoelectronic devices [4], non-linear optical materials [5], etc. and as precursors to SiC ceramics [6]. Much of the recent efforts have been devoted to understand structural variables which effect the energy of the HOMO–LUMO band gap associated with catenated silicon backbone [7]. It has been realized that steric and electronic effects of the side chain substituents such as alkyl/aryl/heteroatom-based groups strongly influence the optoelectronic properties of polysilanes as a

result of conformational changes in the silicon backbone [1,8]. In this context, copolysilanes of the general formula $(\text{R}_2\text{Si})_x(\text{R}'_2\text{M})_y$ ($\text{R} \neq \text{R}'$; $\text{M} = \text{Si}, \text{Ge}, \text{Sn}$) are found to be advantageous relative to the homopolymers, since various physical, mechanical and electronic properties can be tuned in accordance with the nature of monomeric components as well as molecular weight and composition of the resulting polymers [1a,9,10]. In general, copolymers containing higher molar ratio of tin result in a significant bathochromic shift in the UV absorption in comparison to that observed in copolysilane analogs [10]. This may be attributed to effective overlap of orbitals resulting from increased atomic size of tin over silicon [11]. A common approach for the synthesis of such copolymers involves Wurtz coupling of dichlorodiorganosilane precursors or their germanium and tin analogs.

Within the framework of our research interest in polysilane chemistry, we have recently reported a number of unsymmetrical polysilanes $-\text{[RR}'_2\text{Si}(\text{CH}_2)_x\text{SiR}^1]_n-$ ($\text{R}, \text{R}' = \text{Me}, \text{Et}, \text{Ph}$ or H ; $\text{R}^1 = \text{Me}, \text{Ph}, \text{H}$ or carbosilyl; $x = 2$

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or 3) bearing carbosilyl functionalities on the silicon backbone [12]. The primary impetus has been to comprehend the role of appended sila-alkyl groups on the electronic properties associated with σ – σ^* transitions. The presence of sila-alkyl groups on the silicon backbone has also expanded the scope of substitution chemistry for chemical modification of the side chain groups. As a continuation of this work, we have extended these studies to copolysilanes, **1–6** (Scheme 1) bearing $[\text{RR}'_2\text{Si}(\text{CH}_2)_2\text{SiMe}]$ and $[\text{PhMeSi}]/[\text{Ph}_2\text{Si}]$ units in the polymer backbone. The results obtained are reported herein.

2. Results and discussion

2.1. Synthesis of copolysilanes **1–6**

Following Wurtz coupling method, the condensation reaction of $\text{RR}'_2\text{Si}(\text{CH}_2)_2\text{SiMeCl}_2$ and PhMeSiCl_2 or Ph_2SiCl_2 in 1:1 molar ratio has been carried out with sodium dispersion in refluxing toluene (Scheme 1). The reaction conditions such as reaction time, stirring speed and addition time of the monomers are kept constant for each reaction. Effective separation of high molecular weight fraction representing copolysilanes **1–6** from the reaction mixture is accomplished by repeated fractional precipitation using toluene/isopropanol mixture.

2.2. Characterization

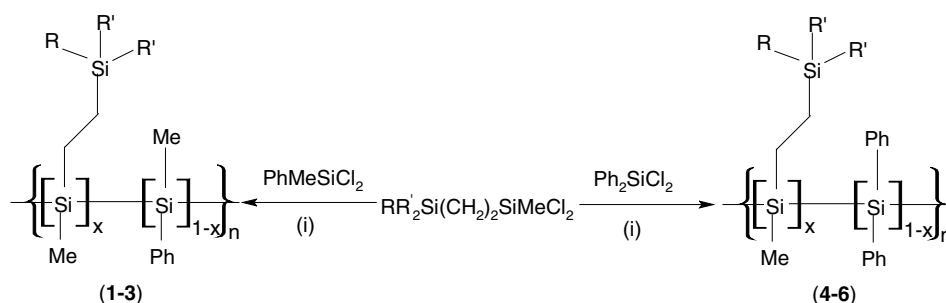
All the polysilanes obtained herein are white solids and are soluble in common organic solvents such as toluene, THF, chloroform, dichloromethane, benzene etc. Thermogravimetric analysis (TGA) reveals that these are stable upto 350–400 °C. However, subsequent weight loss is observed in a continuous manner upto 500 °C leaving a residual yield of 13–35%. An examination of the GPC data (Table 1) reveals high molecular weight with M_w as $(25\text{--}112) \times 10^3$. However, polydispersity values are found to vary depending upon the nature of the monomers used. The high polydispersity (PDI = 4.68–5.49) as observed for **2–4** is not unusual in view of similar precedence in literature for a number of related copolysilanes [9a,10b]. A representative GPC profile of the copolysilane **1** is shown in Fig. 1.

2.3. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra

The ^1H NMR spectrum of each polymer shows broad massifs at δ 1.86 to -1.02 representing the chemical shift domain for aliphatic groups associated with the methyl and appended carbosilyl moiety. The *SiPh* groups resonate at δ 7.25–6.99. Nevertheless, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra reveal well resolved signals and allow the detection of side chain substituents in each polysilane. The assignment of various ^{13}C NMR signals are made by comparison with those observed for related homopolymers [12a]. The relevant data are summarized in Section 3.

2.4. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra

$^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of the copolymers are quite informative and distinctly identify different silicon environments. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of the copolymers **1–3** reveal a singlet at δ 7.73 to -6.48 due to the appended $\text{RR}'_2\text{Si}$ moieties of the carbosilyl groups. The backbone silicon atoms associated with $-\text{[RMeSi]}-$ (R = carbosilyl) units appear at δ -27.26 to -28.10 as a complex pattern of partially resolved peaks arising from stereogenic silicon centers (Fig. 2). The observed chemical shifts are similar to those reported for the corresponding homopolymers [12a]. The spectrum of each polysilane also exhibits three distinct resonances at δ -39.24 to -41.25 due to $-\text{[PhMeSi]}-$ units. By analogy with literature precedence [9c,13], the observed ^{29}Si NMR profile is considered to represent triad level stereodomains, with the exception that the intensity ratio of these signals differ from that observed for poly(methylphenylsilane). For example, the signals at δ -39.37 , -39.85 (for **1**), 39.24 , -39.95 (for **2**) and -39.24 , -39.81 (for **3**) show an enhanced intensity in comparison to the pattern observed for poly(methylphenylsilane). At a first glance, the spectral behavior may simply be attributed to the change in the relative tacticity of the $-\text{[PhMeSi]}-$ segments in the copolymers. The removal of the phenyl group on certain monomer units and displacing the bulky silyl group away from the silicon backbone may simply result in increase in the proportions of hetero and syndiotactic placements, in comparison to the enhanced content of isotactic placements observed for the $-\text{[PhMeSi]}_n-$ homopoly-

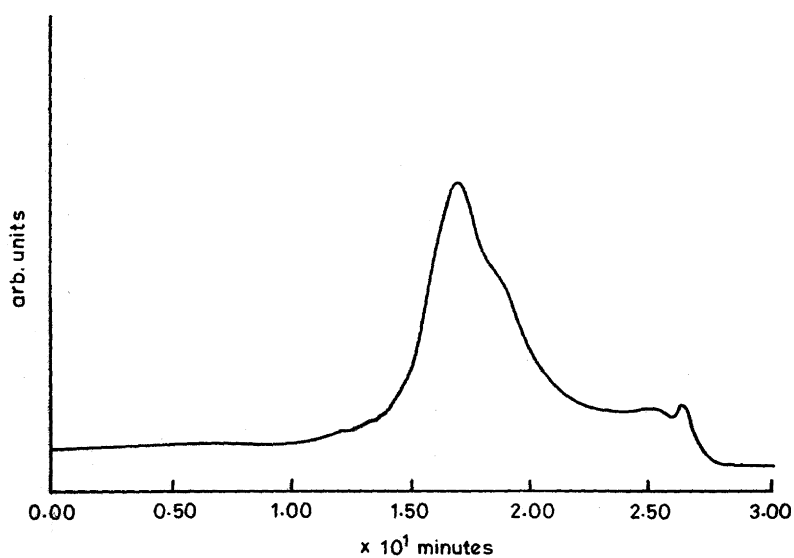
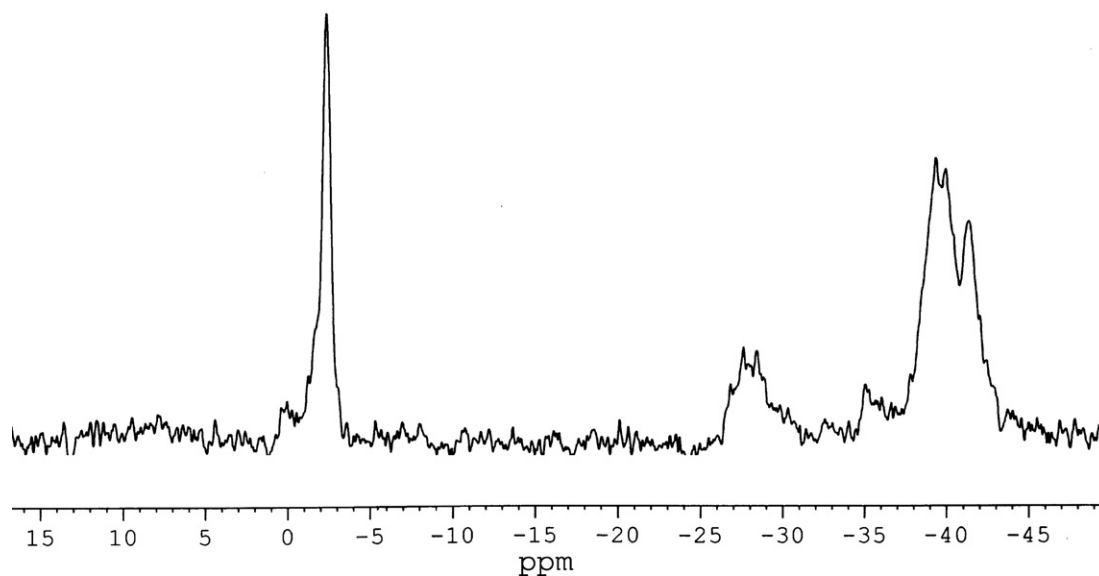


Scheme 1. Reaction conditions: (i) Na, toluene, 110 °C, 4 h R = R' = Et (**1,4**); R = Ph; R' = Me (**2,5**); R = Me; R' = Ph (**3,6**).

Table 1

²⁹Si{¹H} NMR, UV and GPC data of copolymers, {[RR'₂Si(CH₂)₂SiMe]_x[PhR¹Si]_{1-x}]_n (1–6)

Polysilane	RR' ₂ Si/R ¹	x:1 - x ^a	²⁹ Si{ ¹ H} NMR (ppm)	UV ^b λ _{max} /ε	M _w × 10 ^{-3c}	PDI ^d	Yield ^e
1	Et ₃ Si/Me	0.36:0.64	7.73, -28.10, -35.43, -39.37, -39.85, -41.15	312/3100 262	112	1.67	6.5
2	PhMe ₂ Si/Me	0.5:0.5	-2.31, -27.56, -35.03, -39.24, -39.95, -41.25	328/3000 266	58	4.68	9.3
3	Ph ₂ MeSi/Me	0.5:0.5	-6.48, -27.26, -34.91, -39.24, -39.81, -41.11	327/13000 270	25	5.49	10.1
4	Et ₃ Si/Ph	0.34:0.66	7.68, -25.63 to -26.59, -29.03 to -36.78	321/3800 264	50	5.17	7.2
5	PhMe ₂ Si/Ph	0.42:0.58	-2.76, -25.56 to -34.89	352/4400 263	81	1.86	12.1
6	Ph ₂ MeSi/Ph	0.48:0.52	-6.52, -24.01 to -35.00	333/1700 266	81	1.36	15.3

^a Based on ¹H NMR data.^b ε units: (Si repeat unit)⁻¹ dm³ cm⁻¹; λ_{max} units: nm.^c Molecular weights determined by GPC relative to polystyrene standards; eluant: THF; 25 °C.^d PDI = polydispersity index (M_w/M_n).^e Isolated yield of high molecular weight fraction.Fig. 1. GPC profile of {[Et₃Si(CH₂)₂SiMe]_x[PhMeSi]_{1-x}]_n (1).Fig. 2. ²⁹Si{¹H} NMR spectrum of {[PhMe₂Si(CH₂)₂SiMe]_x[PhMeSi]_{1-x}]_n (2).

mer [13]. However, these results are somewhat intriguing if one considers that the configurational sequence of the $-\text{[PhMeSi]}-$ runs in the copolysilanes remains similar to that reported for the homopolymer. Thus, an alternate explanation for the observed enhancement in the signal intensities in **1–3** can be put forth by considering a fortuitous ^{29}Si chemical shift degeneracy between the $-\text{[PhMeSi]}-$ polymeric chains and the PhMeSi units which are adjacent to RMeSi (R = carbosilyl) group (Chart 1). In addition, a low intensity signal at $\delta -35.43$ (**1**); -35.03 (**2**); -34.91 (**3**) has been assigned to RMeSi group with adjacent PhMeSi unit. The spectral data is analogous to those observed for poly(methylphenylsilane)-*co*-poly(hexylmethylsilane) [9c] and suggest long segregated runs of $-\text{[PhMeSi]}-$ and $-\text{[RMeSi]}-$ units in the polysilanes **1–3**. For copolysilanes **4–6** bearing $-\text{[Ph}_2\text{Si]}-$ units, distinct ^{29}Si NMR resonance due to side chain carbosilyl groups appear at their routine position (Table 1). For **4**, the silicon backbone associated with $-\text{[RMeSi]}-$ and $-\text{[Ph}_2\text{Si]}-$ units appear as closely overlapping signals at $\delta -25.63$ to -26.59 and $\delta -29.03$ to -36.78 , respectively (Fig. 3). However, these resonances remain unresolved for **5** and **6** and appear as a broad massif at $\delta -24.01$ to -35.00 , thus suggesting many different configurational and conformational environments of the silicon backbone.

2.5. UV spectral studies

UV spectral studies of copolysilanes **1–6** have been performed to gain insight into the electronic properties associated with σ -delocalized silicon backbone. The UV absorption spectra of the copolysilanes are shown in Figs. 4 and 5 and the relevant spectral data (λ_{max} and ϵ values) are given in Table 1. As expected, these polymers exhibit $\sigma-\sigma^*$ transition with absorption maxima (λ_{max}) lying in the range of 312–352 nm. It is imperative to mention that the pair of polysilanes (**1, 4**); (**2, 5**) and (**3, 6**) possess similar carbosilyl groups but differ in the composition with respect to $[\text{PhMeSi}]/[\text{Ph}_2\text{Si}]$ units. A comparison of the UV spectral data of these pair of polysilanes clearly reveals a distinct bathochromic shift of λ_{max} values for **4–6** bearing $-\text{[Ph}_2\text{Si]}-$ units, the maximum observed differ-

ence being of the order of 24 nm for **2, 5** pair. This allowance in the λ_{max} cannot be justified only by considering the phenyl substitution effects. It is known from the study of substituted oligomeric silane derivatives that the addition of the first aryl substituent produces the most striking spectral changes due to $\sigma-\pi$ mixing [14]. However, subsequent incorporation of additional geminal aryl substituents results in minimal changes in the λ_{max} value, although the intensity of transition often increases. Therefore, a plausible explanation for the observed electronic spectra for the copolysilanes **2** and **5** may come from a consideration of conformational effects of the silicon backbone. It is believed that presence of two bulky geminal phenyl substituents in polysilane **5** favors a more extended *trans* conformation in solution and results in discernable bathochromic shift in the λ_{max} value. Although a similar dependence of λ_{max} values has been observed for other pair of polysilanes, the effect seems to be much less pronounced.

A scrutiny of the spectral data of the polysilanes **1–3** as well as **4–6** reveals that copolymers bearing sterically bulky $\text{PhMe}_2\text{Si}/\text{Ph}_2\text{MeSi}$ moiety on the carbosilyl side chain exhibit higher λ_{max} values when compared with Et_3Si -substituted polysilanes. These results suggest a significant dependence of $\sigma-\sigma^*$ transition on the nature of the appended sila-substituents and correlates well with our earlier studies on carbosilyl-substituted polysilanes prepared by Wurtz coupling method [12a]. However, a careful scrutiny of the spectral data (Table 1) reveals that the copolymer **3** shows a marked increase in the molar absorptivity (ϵ) value while the λ_{max} values observed for copolysilanes **5** and **6** are not in conformity with the steric effect of the appended PhMe_2Si and Ph_2MeSi groups, respectively. It is thus believed that other variables such as copolymer composition and comonomer sequence may also have significant contribution in influencing the electronic properties of these copolysilanes [9f].

In summary, the copolysilanes, $\{[\text{RR}'_2\text{Si}(\text{CH}_2)_2\text{SiMe}]_x-\text{[PhR}_1\text{Si}]_{1-x}\}_n$ (**1–6**) (R, R' = Me, Et or Ph; R¹ = Ph or Me) reported herein differ from the known copolysilanes in view of the inclusion of functionally substituted carbosilyl groups. The steric influence of these groups on the

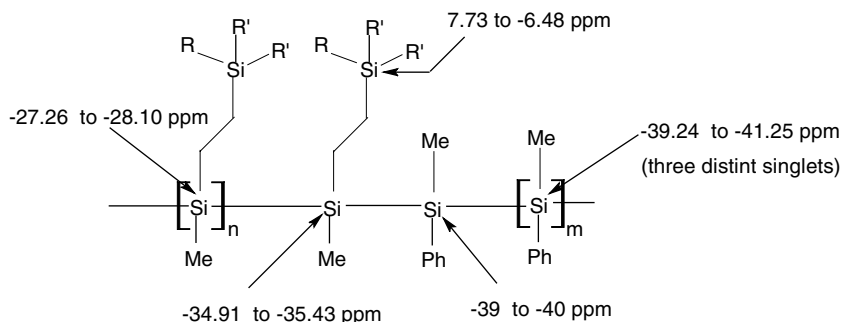


Chart 1.

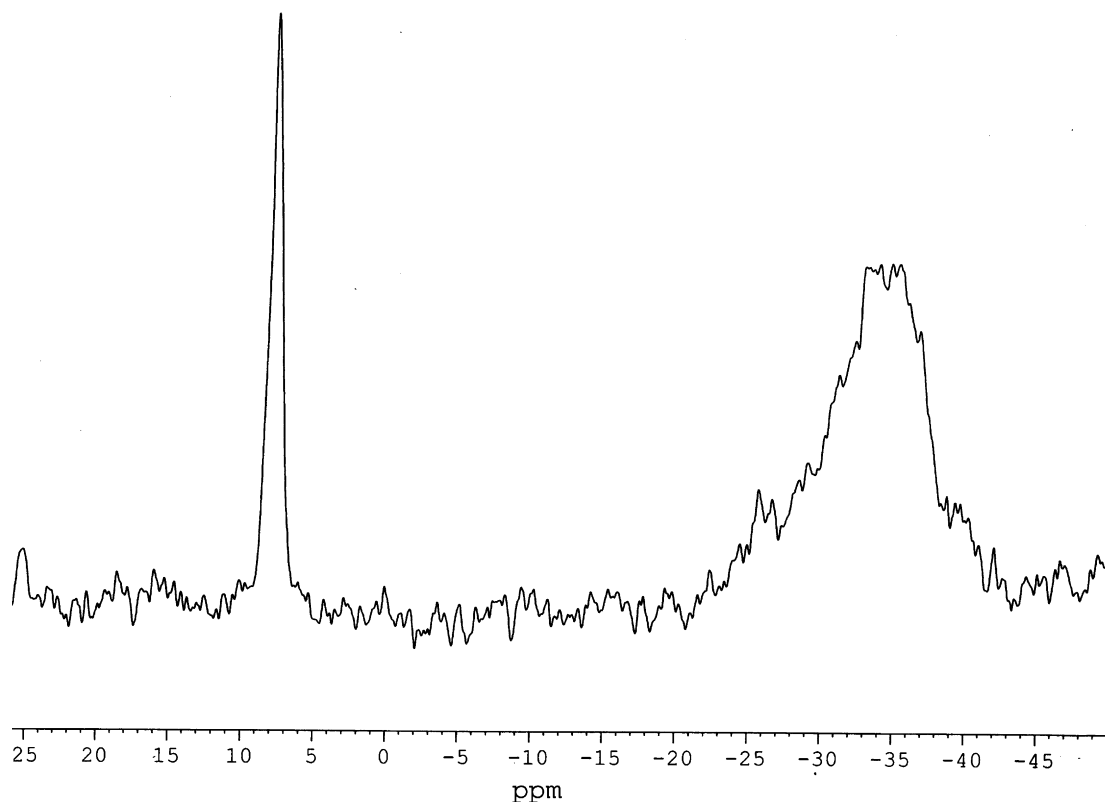


Fig. 3. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of $\{[\text{Et}_3\text{Si}(\text{CH}_2)_2\text{SiMe}]_x[\text{Ph}_2\text{Si}]_{1-x}\}_n$ (4).

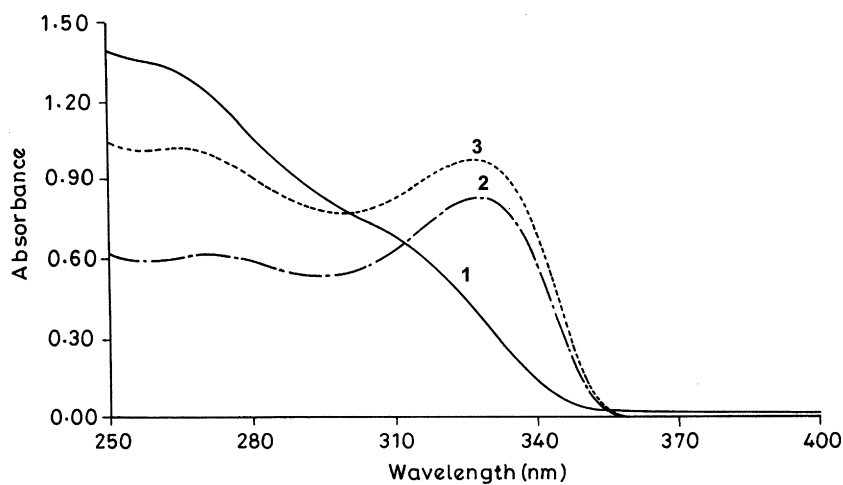


Fig. 4. UV spectra (THF, RT) of polysilanes 1–3.

electronic properties associated with $\sigma\text{--}\sigma^*$ transition of the silicon backbone is clearly evident in their UV spectra. A detailed analysis of $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of the copolymers 1–3 reveal that silicon backbone is comprised of segregated runs of PhMeSi and RSiMe ($\text{R} = \text{carbosilyl}$) units. Similar studies on the copolymers 4–6 bearing Ph_2Si units suggest many different configurational and conformational environments.

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 (tetrahydrofuran, toluene) or magnesium

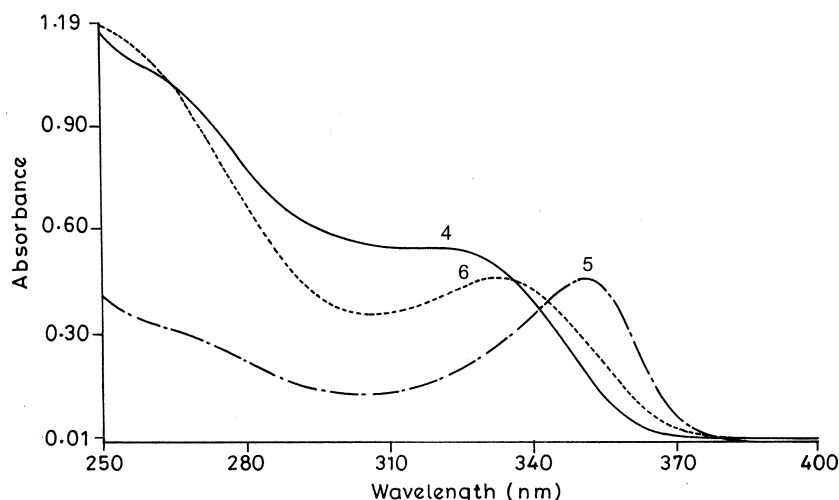


Fig. 5. UV spectra (THF, RT) of polysilanes 4–6.

(alcohols) before use. Glasswares were dried in an oven at 100–120 °C and further flame dried under vacuum prior to use. The dichlorocarbosilanes used herein are prepared by following the earlier procedure [12a].

Infrared spectra were obtained as thin films on KBr pellets on a Nicolet FT-IR (Protégé) spectrometer. UV spectra were recorded on a Perkin–Elmer (Lambda 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. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra were recorded in CDCl_3 on Bruker spectropin DPX 300 MHz instrument at frequency 300, 75.5, 59.6 MHz, respectively and chemical shifts are quoted relative to Me_4Si . Thermogravimetric analysis of polysilanes 1–6 was carried out in N_2 atmosphere between 30 and 800 °C heating rate 10 °C/min on a Perkin–Elmer Thermal analysis system.

3.2. Preparation of copolysilanes 1–6

In a typical procedure, freshly weighed sodium (1.5 g, 65.21 mmol) was transformed to a fine dispersion in refluxing toluene under dry nitrogen atmosphere and a solution of dichlorocarbosilane, $\text{Et}_3\text{Si}(\text{CH}_2)_2\text{SiMeCl}_2$ (3.85 g, 15.00 mmol) and phenylmethyldichlorosilane (2.87 g, 2.44 mL, 15.00 mmol) was added dropwise into it. The reaction mixture turned deep blue in color and the contents were allowed to reflux at 110 °C for 4 h. The resulting solution was then filtered under nitrogen and the solvent was stripped off from the filtrate to afford a crude polymer. The high molecular weight copolysilane 1 was obtained as solid by careful centrifugation of the crude product using toluene/isopropanol mixture. The copolysilanes 2 and 3 were obtained similarly by reacting equimolar quantity of the corresponding dichlorocarbosilane, $\text{RR}'_2\text{Si}(\text{CH}_2)_2\text{SiMeCl}_2$ ($\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$) and phenylmethyldichlorosilane in presence of sodium dispersion.

The synthetic procedure for copolysilanes 4–6 is similar to that described above for 1–3. The dichlorocarbosilanes, $\text{RR}'_2\text{Si}(\text{CH}_2)_2\text{SiMeCl}_2$ [$\text{R} = \text{R}' = \text{Et}$; $\text{R} = \text{Ph}$, $\text{R}' = \text{Me}$; $\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$] (20.00 mmol) and diphenyldichlorosilane (20.00 mmol) were used as the starting materials. For assigning the NMR spectral data, methylene group attached to SiMe moiety is represented with the notation, (α -) and subsequent methylene is designated with β -notation.

3.2.1. $\{[\text{Et}_3\text{Si}(\text{CH}_2)_2\text{SiMe}]_x[\text{PhMeSi}]_{1-x}\}_n$ (1)

^1H NMR: δ 7.28 (br, SiPh), 0.96 (br, $\text{CH}_3\text{-Et}$), 0.55 (br, α - and β - CH_2 + $\text{CH}_2\text{-Et}$) 0.20 (br, SiMe). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 136.82, 134.87, 133.24, 127.62 (SiPh), 8.95 (α - CH_2), 7.43 ($\text{CH}_3\text{-Et}$), 6.38 (β - CH_2), 2.84 ($\text{CH}_2\text{-Et}$), -5.94 (SiMe).

3.2.2. $\{[\text{PhMe}_2\text{Si}(\text{CH}_2)_2\text{SiMe}]_x[\text{PhMeSi}]_{1-x}\}_n$ (2)

^1H NMR: δ 7.25 (br, SiPh), 1.86 to -0.81 (br, alkyl region). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 137.15, 134.23, 128.68, 127.46 (Si-Ph), 10.48 (β - CH_2), 9.23 (α - CH_2), 2.95 (Ph Me_2Si), -5.12 (SiMe).

3.2.3. $\{[\text{Ph}_2\text{MeSi}(\text{CH}_2)_2\text{SiMe}]_x[\text{PhMeSi}]_{1-x}\}_n$ (3)

^1H NMR: δ 7.31 (br, SiPh), 1.25 to -1.02 (br, alkyl region). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 137.03, 134.29, 128.95, 127.63 (Si-Ph), 9.66 (β - CH_2), 6.94 (α - CH_2), -4.72 (Ph $_2\text{MeSi}$), -5.06 (SiMe).

3.2.4. $\{[\text{Et}_3\text{Si}(\text{CH}_2)_2\text{SiMe}]_x[\text{Ph}_2\text{Si}]_{1-x}\}_n$ (4)

^1H NMR: δ 7.04 (b, SiPh), 0.68, 0.22 (br, alkyl region). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 136.75, 134.29, 127.56 (Si-Ph), 9.01 (α - CH_2), 7.45 ($\text{CH}_3\text{-Et}$), 6.43 (β - CH_2), 2.77 ($\text{CH}_2\text{-Et}$), -3.02 (SiMe).

3.2.5. $\{[\text{PhMe}_2\text{Si}(\text{CH}_2)_2\text{SiMe}]_x[\text{Ph}_2\text{Si}]_{1-x}\}_n$ (5)

^1H NMR: δ 7.25, 6.99 (br, SiPh), 0.56 to -0.52 (br, alkyl region). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 137.02, 134.77, 134.43, 128.99, 127.68 (Si-Ph), 10.48 (β - CH_2), 9.23 (α - CH_2), 2.95 (Ph Me_2Si), -5.12 (SiMe).

3.2.6. $\{[Ph_2MeSi(CH_2)_2SiMe]_x[Ph_2Si]_{1-x}\}_n$ (6)

1H NMR: δ 7.18 (br, SiPh), 1.25 to -0.75 (br, alkyl region). $^{13}C\{^1H\}$ NMR: δ 137.02, 134.77, 134.43, 128.99, 127.68 (Si–Ph), 9.33 (β -CH₂), 5.86 (α -CH₂), -5.15 (Ph₂MeSi), -6.11 (SiMe).

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