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# Synthesis, Characterization, and Photoluminescence Properties of Asymmetrically Substituted Functional Polysilanes Bearing Carbosilyl Side Chains, $-[R(Me)Si]_n-$ and $-[R(Ph)Si]_n-$ $[R = (CH_2)_xSiR'_3;$ $x = 2$ or $3]$

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ABSTRACT: New unsymmetrical polysilanes, $-[R^1(Me)Si]_n-$ (**1**−**3**), $-[R^2(Me)Si]_n-$ (**4**−**6**), and $-[R^2(Ph)Si]_n-$ (**7**−**9**), bearing pendant sila-substituted alkyl groups of varying chain length [$R^1$: $(CH_2)_3Si\equiv$; $R^2$: $(CH_2)_2Si\equiv$] have been synthesized by Wurtz coupling reaction. These polysilanes reveal a monomodal molecular weight distribution with $M_w$ in the range $(237-31) \times 10^3$ for **1**−**6** and $(2.9-2.3) \times 10^3$ for **7**−**9**. Stereochemical configuration of polysilane **2** has been deduced from a detailed analysis of $^{13}C\{^1H\}$ NMR resonances of backbone Si−Me groups and suggests a predominantly atactic microstructure. UV absorption spectra of polysilanes **1**−**3** ($\lambda_{max}$: 303−317 nm; $\epsilon$: 2800−5900 (Si repeat unit)$^{-1}$ dm$^3$ cm$^{-1}$) feature a discernible bathochromic shift and higher extinction coefficient values in comparison to those observed for analogous polysilanes **4**−**6** ($\lambda_{max}$: 296−305 nm; $\epsilon$: 2000−3000 (Si repeat unit)$^{-1}$ dm$^3$ cm$^{-1}$). These results coupled with photoluminescence (PL) spectra indicate that electronic properties of these polysilanes are influenced by the pendant sila-alkyl chain length as well as by steric effect of substituents on a silicon atom. UV and PL emission and excitation spectral characteristics of phenyl-substituted polysilanes **7**−**9** provide evidence in favor of $^1(\sigma-\pi^*)^{CT}$ charge-transfer phenomenon.

## Introduction

During the past two decades, research interest in the domain of polysilane chemistry has been largely focused to understand their unique electronic and optical properties associated with $\sigma$ conjugation in the catenated silicon backbone.[1] These intrinsic properties make polysilanes promising candidates for various applications such as photoresists,[2] optoelectronic devices,[3] and nonlinear optical materials.[4]

The occurrence of $\sigma-\sigma^*$ electronic transition in polysilanes is manifested by an intense absorption in the UV region (270−400 nm). It is now well established that the energy of this electronic absorption has a strong dependence on the conformational characteristics of catenated silicon backbone. Significant influence of side-chain alkyl/aryl substituents in tailoring conformational features of the backbone structure and consequently its optoelectronic properties are also well documented.[1,5,9d] A distinct manifestation of this structure−property relation appears from a number of interesting thermochromic studies in symmetrically and asymmetrically substituted poly(di-*n*-alkylsilane)s[1,6] representing compositional formulas $-[R_2Si]_n-$ and $-[RR'Si]_n-$ ($R \neq R'$ = alkyl), respectively. These polysilanes undergo either a gradual (continuous) or an abrupt (discontinuous) shift of the absorption band to longer wavelength as temperature is lowered. A theoretical explanation of thermochromic behavior in polysilanes has been put forth by Schweizer.[7] It has been suggested that dispersive interactions of $\sigma$-delocalized electrons along the backbone with pendant side chains induce conformational changes at variable temperatures, and the magnitude of these interactions triggers a bathochromic shift in the UV spectra.[6d,g]

The quasi-one-dimensional nature of polysilanes with delocalized $\sigma$-conjugated electrons imparts photoluminescence (PL) properties with high quantum efficiency, usually in near-UV or UV region.[1a,5d,8] In this respect, poly(alkyl−arylsilane)s are found to differ from those of poly(di-*n*-alkylsilane)s. For example, poly(methylphenylsilane) exhibits a broad photoluminescent band in the visible region (VPL), in addition to a strong excitonic UV photoluminescence (UPL) at ca. 320 nm associated with the $\sigma-\sigma^*$ transition.[9,10] The origin of VPL is generally ascribed to branching defects in the polymer chain which can be caused by photodecomposition of the polymer and insertion of silyl radicals in the backbone. However, a detailed study of temperature-dependent photoluminescence spectra of poly(methylphenylsilane) has shown that the emission band in the visible region (VPL) is attributed to polymer branching as well as $^1(\sigma-\pi^*)^{CT}$ charge-transfer transitions.[10] The disappearance of the VPL band is executed in poly(alkylarylsilane)s, $-[R(Ph)Si]_n-$ (R = pentyl or higher alkyls) with long chain alkyl substituents.[9b,c] It has been proposed that steric effect of these groups favors decomposition at the branching sites as a result of thermal reactions and leads to linear polysilanes with minimal branching defects.

Although extensive studies related to structure and electronic properties of poly(di-*n*-alkylsilane)s have been reported, much less attention has been devoted to address the influence of heteroatom-substituted alkyl chains bonded to skeletal silicon backbone. There are a few previous reports that describe the synthesis of polysilanes bearing polar ether linkage in the pendant alkyl groups.[11] These polysilanes exhibit interesting physical and electronic properties which differ from those of *n*-alkyl-substituted polysilane analogues. The present paper describes synthesis and characterization of new unsymmetrical polysilanes, $-[R^1(Me)Si]_n-$ (**1**−

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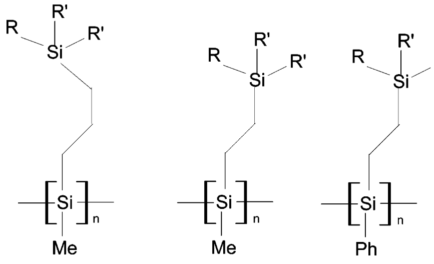
**Scheme 1**



R = R' = Et (**1, 4, 7**)
R = Ph; R' = Me (**2, 5, 8**)
R = Me; R' = Ph (**3, 6, 9**)

**3**), $-[R^2(Me)Si]_n-$ (**4**−**6**), and $-[R^2(Ph)Si]_n-$ (**7**−**9**) [ $R^1$: $(CH_2)_3Si\equiv$; $R^2$: $(CH_2)_2Si\equiv$] bearing pendant carbosilyl groups of varying alkyl chain length (Scheme 1). These polymers can be regarded as analogues of extensively studied poly(methyl-*n*-alkylsilane)s or poly(phenyl-*n*-alkylsilane)s with the exception that the $\beta$- or $\gamma$-carbon of the alkyl chains possesses sterically demanding sila-substituted groups. Since structural characteristics of silaalkanes are known to differ from those of corresponding *n*-alkanes,[12] it was of interest to examine the influence of pendant carbosilyl groups on the electronic properties of these new polysilanes. The results obtained from these studies are reported herein.

## Results and Discussion

**Synthesis and Characterization of Polysilanes, 1**−**9.** Following the classical Wurtz coupling method,[1] reactions of dichlorocarbosilane precursors, $Me(RR_2'SiCH_2CH_2CH_2)SiCl_2$ (**1a**−**3a**), $Me(RR_2'SiCH_2CH_2)SiCl_2$ (**4a**−**6a**), or $Ph(RR_2'SiCH_2CH_2)SiCl_2$ (**7a**−**9a**) [R, R′ = Et, Me, or Ph], with sodium dispersion in refluxing toluene afford a crude polymer in each case having both low and high molecular weight fractions. Effective separation of the corresponding high molecular weight polysilanes **1**−**9** (Scheme 1) from the crude mixture is accomplished by repeated fractional precipitation using a toluene/2-propanol mixture. The formation of these polysilanes in low yield (5−15%) is not unusual in view of the known limitations of the Wurtz coupling method. Using this approach, it is generally observed that sterically demanding monomers afford low molecular weight polysilanes with poor yields.[1a,9c,13]

All the polysilanes obtained herein are either viscous gums (**1**−**6**) or solids (**7**−**9**) and are soluble in common organic solvents such as toluene, THF, hexane, chloroform, dichloromethane, benzene, etc. Thermogravimetric analysis (TGA) reveals that these are stable up to 370−400 °C. However, subsequent weight loss is observed in a continuous manner up to 500 °C, leaving a residual yield of 7−18%. GPC analysis of these polysilanes (Table 1) reveals a monomodal molecular weight distribution in each case with $M_w$ ranging between $(237-31) \times 10^3$ for **1**−**6** and $(2.9-2.3) \times 10^3$ for **7**−**9**. A representative GPC profile of polysilane **2** is shown in Figure 1. The chemical composition of each polymer has been elucidated by IR and multinuclear NMR studies. A notable feature in the IR spectra of polysilanes **7**−**9** is the appearance of a weak intensity band at 2083−2090 $cm^{-1}$ due to $\nu_{SiH}$ end groups. By analogy with earlier reports,[14] the formation of Si−H groups during Wurtz coupling is attributed to abstraction of hydrogen from the solvent by silyl radicals. However, these groups are not discernible in the spectra of polysilanes **1**−**6** due to their high molecular weights. The $^1H$ NMR spectrum ($CDCl_3$, RT) of each polysilane reveals 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 also observed in $^{13}C\{^1H\}$ NMR spectra with the pendant silyl substituents featuring relatively sharp resonances (see Experimental Section). The spectral behavior shows a close analogy with those of poly(methyl-*n*-alkylsilane)s,[15] and the unresolved $^1H$ and $^{13}C\{^1H\}$ resonances of methylene groups may accordingly be attributed to short spin−spin relaxation time of these nuclei. $^{13}C\{^1H\}$ NMR spectra of polysilanes **2**, **3**, **6**, and **7** reveal overlapped or closely spaced signals for methylene carbons as well as for pendant and backbone Si−Me groups. Unequivocal assignments of these signals are made from DEPT-135 $^{13}C\{^1H\}$ and HSQC ($^1H-^{13}C$) NMR spectra, and the results are summarized in the Experimental Section. A common feature in the $^{29}Si\{^1H\}$ NMR spectra of polysilanes **1**−**3** and **6**−**9** is the appearance of a sharp singlet at $\delta$ 8.68 to −7.93 and a broad featureless signal at −25.89 to −31.71. By analogy with the spectral data of the precursor carbosilanes as well as related poly(methyl/phenyl-*n*-alkylsilane)s,[9c,15,16] the former chemical shift value is ascribed to the carbosilyl side groups and the latter to silicon backbone. For polysilanes **4** and **5**, two distinct $^{29}Si\{^1H\}$ NMR signals appear in the carbosilyl region at $\delta$ 8.48, 7.84 and 0.42, −1.32, respectively, and are corroborated with the presence of both $\alpha$ (minor) and $\beta$ (major) isomers in the precursor dichlorocarbosilanes. The NMR spectral data coupled with GPC results clearly indicate that all the polysilanes are devoid of oligomeric/cyclic products.

**Configurational Studies.** In principle, unsymmetrical polysilanes may adopt the isotactic (all meso, mm), syndiotactic (all racemic, rr), or atactic (random, rm/mr) configuration.[17] It has been reported by Schilling et al.[15] that the stereochemical configuration of poly(methyl-*n*-alkylsilane)s can be estimated using $^{13}C\{^1H\}$ NMR spectroscopy, since methyl groups bonded to the skeletal backbone respond to configurational characteristics. In the $^{13}C\{^1H\}$ NMR spectrum of polysilane **2**, three closely spaced resonances at $\delta$ −3.62, −3.74, and −3.92 due to Si−Me (backbone) are distinctly observed and suggest the sensitivity of the nuclei toward configurational sequence. Therefore, a detailed microstructure analysis of the polymer has been performed by deconvolution of the spectral region (Figure 2). The difference between actual and calculated spectra matched within 1% error. The signal at $\delta$ −3.62 was tentatively assigned to the rr stereodomain while the high field resonances at $\delta$ −3.74 and −3.92 were subscribed to rm/mr and mm stereodomains, respectively. On the basis of deconvolution studies, the signal intensity of each chemical shift region was deduced, and the intensity of the triad domain (rr:rm/mr:mm) has been evaluated as 0.44:0.45:0.10. A good agreement between these values and those predicted by Bernoullian statistics[18] (0.46:0.43:0.10) is observed with Pm = 0.32 and Pr = 0.68. These results suggest that the polysilane adopts a predominantly atactic configuration with a syndiotactic bias. It is however imperative to mention that the interchange in $\delta$ $^{13}C$ assignments of rr and mm configuration will not affect the Bernoullian statistics but will result in isotactic preference of the configuration. The

**Table 1. UV/Photoluminescent Spectral Data and GPC Characteristics of Polysilanes 1−9**

| polysilane | UV[a] $\lambda_{max}/\epsilon$/fwhm | PL(emission)[b] $\lambda_{max}$(nm)/fwhm | PL(excitation)[c]$\lambda_{max}$(nm) | $M_w$[d] × $10^{-3}$ | PDI[e] | yield (%)[f] |
|---|---|---|---|---|---|---|
| **1** | 303/2800/34 | 336/22 | | 85 | 1.64 | 6.3 |
| **2** | 314/5900/36 | 336/22 | | 237 | 1.82 | 7.2 |
| **3** | 317/5800/34 | | | 119 | 1.57 | 10 |
| **4** | 296/2000/38 | | 31 | 1.76 | 5.1 | |
| **5** | 304/3000/30 | 336/25 | | 123 | 1.77 | 9.8 |
| **6** | 305/2500/30 | 330/25 | | 146 | 1.55 | 11.7 |
| **7** | 325/1900/26 | 354/28 | (258, 285, 324)[cx] | 2.8 | 1.30 | 8.8 |
| | 265 | 368/30 | (260, 298)[cy] | | | |
| **8** | 321/2400/24 | 354/28 | (256, 280, 331)[cx] | 2.9 | 1.30 | 5.8 |
| | 262 | 358/30 | (258, 280, 320)[cy] | | | |
| **9** | 325/2100/29 | 360/34 | (260, 283, 322)[cx] | 2.3 | 1.18 | 12.5 |
| | 265 | 370/36 | (262, 290)[cy] | | | |

[a] $\epsilon$ units: (Si repeat unit)$^{-1}$ dm$^3$ cm$^{-1}$; $\lambda_{max}$ units: nm; fwhm = full width (nm) at half-maximum of $\lambda_{max}$. [b] Peak position in emission spectrum. [c] Peak position in excitation spectrum ([cx]monitored at 370 nm; [cy]470 nm). [d] Molecular weights determined by GPC relative to polystyrene standards; eluant: THF; 25 °C. [e] PDI = polydispersity index ($M_w/M_n$). [f] Isolated yield of high molecular weight fraction.

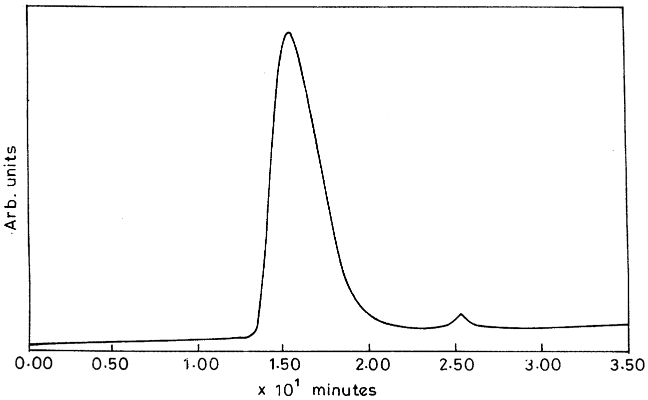


**Figure 1.** GPC profile of $-[Ph_2MeSiCH_2CH_2CH_2SiMe]_n-$ (**3**).

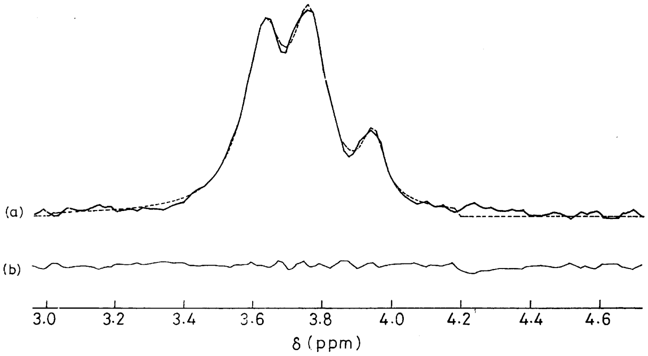


**Figure 2.** Partial $^{13}C\{^1H\}$NMR spectrum of $-[PhMe_2SiCH_2CH_2CH_2SiMe]_n-$ (**2**) depicting Si−*Me* (backbone) region: (a) spectrum (solid line) and calculated spectrum (dotted line); (b) difference between actual and calculated spectrum.

results are in accord with those observed earlier for poly(di-*n*-alkylsilane)s prepared by Wurtz coupling method.[15,19] Unfortunately, configurational analysis for polysilanes **1**, **3**, and **6** could not be made due to either broadening or overlapping of signals associated with pendant and/or backbone Si−Me groups, while similar studies for **4** and **5** are precluded due to presence of α and $\beta$ isomeric mixtures.

**UV and Photoluminescence Spectra.** UV and photoluminescence spectral studies of polysilanes **1**−**6** have been performed to gain insight into the electronic properties associated with $\sigma$-delocalized silicon backbone. The UV absorption spectra (THF, RT) of these polysilanes are shown in Figure 3, and the relevant data are summarized in Table 1. As expected, the observed spectral characteristics such as absorption maxima, absorptivity, and full width at half-maxima values are

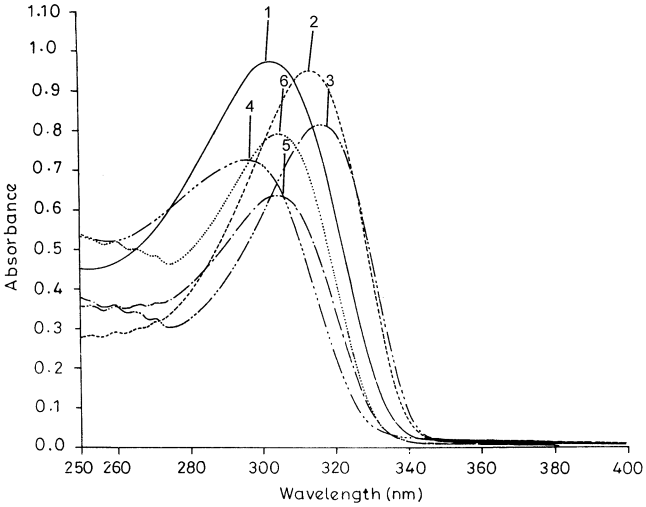


**Figure 3.** UV spectra (THF, RT) of polysilanes **1**−**6**.

quite typical of poly(methyl-*n*-alkylsilane)s.[1,5b,6c] However, a close examination of these results reveal a few notable features. The spectra of polysilanes **2** and **3** bearing a $PhMe_2Si/Ph_2MeSi$ group on the pendant alkyl chains exhibit $\lambda_{max}$ values at higher wavelengths (314, 317 nm) with considerable increase in UV absorptivity ($\epsilon$: 5900, 5800 (Si repeat unit)$^{-1}$ dm$^3$ cm$^{-1}$) when compared with similar parameters of the corresponding $Et_3Si$-substituted polysilane **1** ($\lambda_{max}$: 303 nm; $\epsilon$: 2800 (Si repeat unit)$^{-1}$ dm$^3$ cm$^{-1}$). A similar dependence of the spectral properties on the sila substituents is also seen in polysilanes **4**−**6**, though the effect appears to be much less pronounced. A plausible explanation for this apparently low response of substituent effect on the spectral variations can be made by a close inspection of the spectral data of analogous polysilanes **1**, **4**, **2**, **5**, and **3**, **6** which possess identical silyl groups but differ with respect to the pendant alkyl chain length. Interestingly, a considerable increase in the absorption maxima and absorptivity values is observed in polysilanes **1**−**3** bearing pendant $CH_2CH_2CH_2$ groups in comparison to those observed for corresponding polysilanes **4**−**6** which possess $CH_2CH_2$ groups in the carbosilyl chain. On the basis of these results, it is thus reasonable to conclude that the electronic properties of these polysilanes are sensitive not only to steric influence of the pendant sila substituents but also to the alkyl chain length of carbosilyl groups.

The UV spectral behavior of a number of polysilanes bearing linear and/or branched alkyl chains have been extensively studied in the past. It has been observed

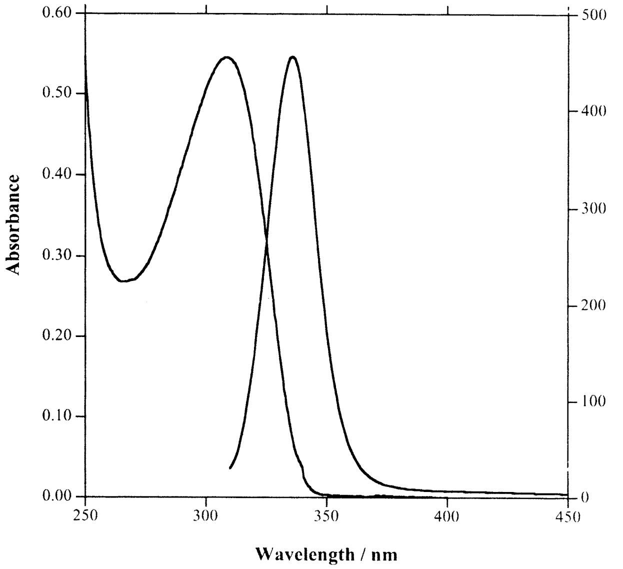


**Figure 4.** UV and PL spectra (THF, RT) of $-[PhMe_2SiCH_2CH_2CH_2SiMe]_n-$ (**2**).

that the absorption maxima are quite sensitive to distinguish low molecular weight linear/cyclic oligomers from high molecular weight polysilanes. Nevertheless, the spectral parameter remains almost constant as the degree of polymerization attains a critical value.[1a] In polysilanes **1**–**6**, this effect appears to be of much less significance in view of their high molecular weights. In addition, there exists a significant correlation between the global conformations of polysilanes and their UV absorption behavior. Depending on the nature of pendant substituents, poly(di-*n*-alkylsilane)s are known to adopt varying conformations which are generally classified as shrink coil, flexible coil, stiff, or rigid-rod-like structures.[5b] This substituent effect is apparently due to steric interference between pendant groups either 1,2 or 1,3 to each other which can result in the change of equilibrium content of trans and gauche conformations in the silicon backbone. In accordance with these trends, the spectral behavior of polysilanes **1**–**6** appear to correspond to a more likely random coil conformation. For polysilanes **2** and **3**, the higher values of absorption maxima and increased absorptivity may result from a cumulative effect of the long alkyl chain and steric influence of the silyl substituents which impart more extended trans conformation to the silicon backbone in solution. Further elaboration of the electronic behavior of polysilanes **1**–**6** has been made from photoluminescence spectra. The UV and PL spectra (THF, RT) for polysilane **2** are shown in Figure 4 as an illustration. As evident from Table 1, PL spectral characteristics of the polysilanes **1**, **2** and **5**, **6** are quite similar and are reminiscent of the Stokes shift of 22–33 nm with full width at half-maxima corresponding to 22–25 nm. In addition, the observed emission profiles are not mirror images of the corresponding UV absorption spectra. These results resemble closely with those of unsymmetrical poly(methyl-*n*-alkylsilane)s[5b,d] which are known to adopt random coil conformational features in solution.

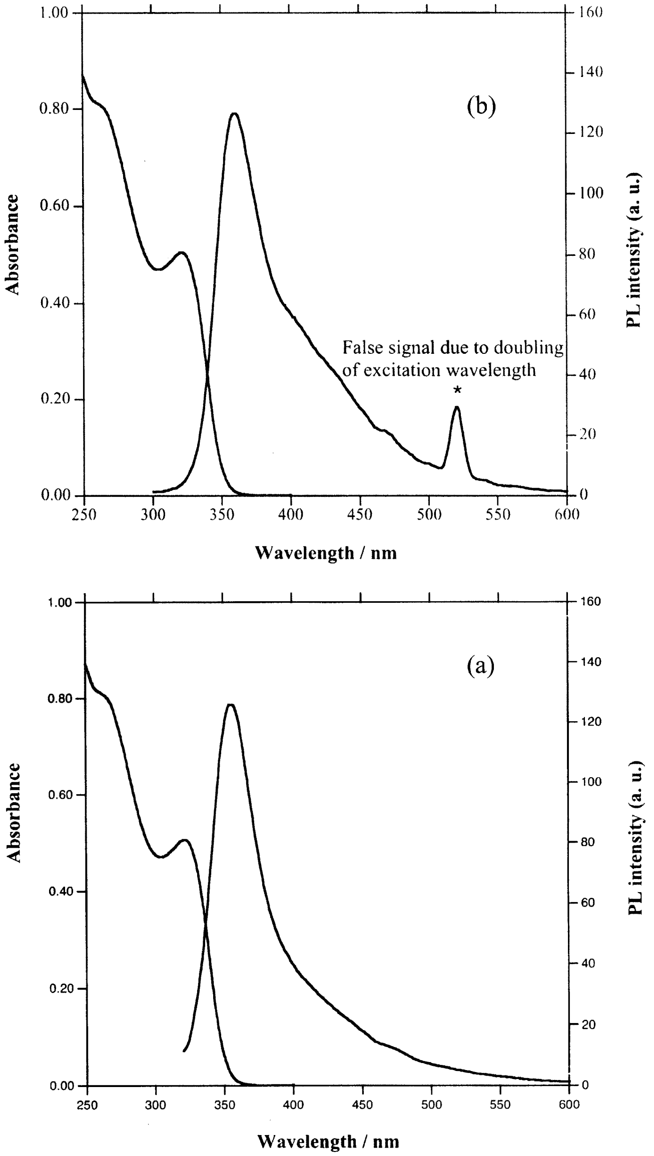


**Figure 5.** UV and PL spectra (THF, RT) of $-[PhMe_2SiCH_2CH_2SiPh]_n-$ (**8**): (a) excitation $\lambda_{max}$ = 315 nm; (b) excitation $\lambda_{max}$ = 260 nm.

The UV and PL spectra of polysilanes **7**–**9** bearing phenyl groups on the silicon backbone differ significantly from those of methyl-substituted polysilane analogues, **4**–**6**. The UV spectrum of each polymer typically shows two absorptions with $\lambda_{max}$ at 321–325 and 262–265 nm which are attributed to $\sigma$–$\sigma^*$ transition of silicon backbone and $\pi$–$\pi^*$ transition of phenyl ring, respectively. The photoluminescence spectra reveal a narrow band at 354–370 nm, which tails in the visible region (VPL) with an edge at ca. 500 nm (Figure 5). It is noteworthy that intensity of the VPL band is weakened upon using 315 nm as the excitation wavelength ($\sigma$–$\sigma^*$ transition) in comparison to that obtained with the excitation at $\lambda_{ex}$ = 260 nm ($\pi$–$\pi^*$). Similar results have been reported earlier for a number of poly(phenyl-*n*-alkylsilane)s, and the origin of the VPL band has been correlated with the presence of branching defects caused by photodecomposition of the polymer and insertion of resulting silylene radicals into the backbone.[9,10] Such structural defects in the silicon chain have also been substantiated by the appearance of additional $^{29}$Si NMR signals around $\delta$ −35 and −45. However, an examination of $^{29}Si\{^1H\}$ NMR spectra of polysilanes **7**–**9** does not reveal additional signals associated with branched chains. It is believed that the low concentration of branching defects, if present in these polysilanes, may have eluded detection on the NMR scale.

An alternate explanation for the origin of VPL band involving charge transfer state $^1(\sigma-\pi^*)^{CT}$ has also been put forth by a detailed study of the excitation spectra

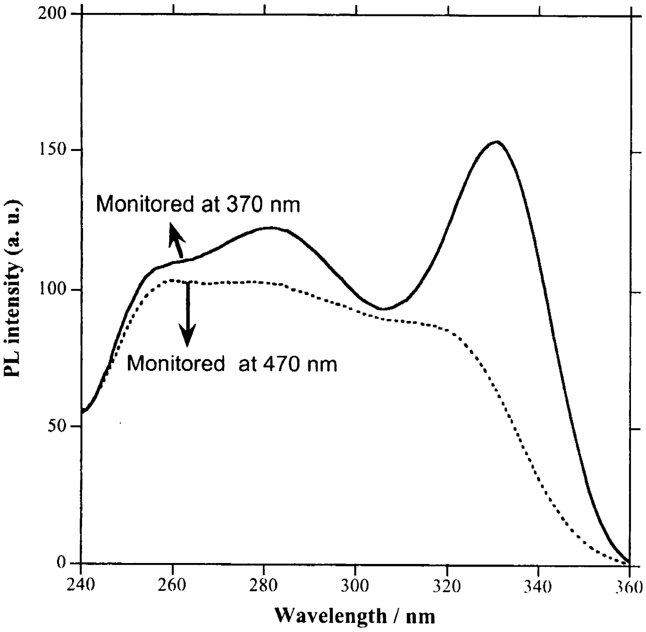


**Figure 6.** Excitation spectra of $-[PhMe_2SiCH_2CH_2SiPh]_n-$ (**8**) monitored for UPL at 370 nm (solid line) and VPL at 470 nm (dotted line).

of poly(methylphenylsilane) thin films monitored at low temperatures.[10] In line with these findings, the excitation spectra of polysilanes **7**−**9** have been studied to further elaborate the results of PL spectra. As shown in Figure 6, the excitation spectrum of polysilane **8** monitored at $\lambda_{max} = 370$ nm (UPL) reveals three distinct optical transitions at 256, 280, and 331 nm. While the peaks at 256 and 331 nm are similar to those observed in the absorption spectrum, the band at 280 nm shows a new appearance. Significantly, the excitation spectrum of VPL monitored at $\lambda_{max} = 470$ nm also exhibits these transitions. The spectra of polysilanes **7** and **9** reveal a similar profile as that of **8** except that the excitation monitored at 470 nm shows a considerable broadening of the band at 290−298 nm. The appearance of new band at 280−298 nm in both the UPL and VPL has not been clearly understood, although the results are in accord with recent photoluminescence studies of poly(methylphenylsilane) by Nešpůrek et al.[10] These authors have proposed that the origin of the new band can be associated with the formation of interchain charge transfer state $^1(\sigma-\sigma^*)^{CT}$ which is located at a higher energy than Frenkel exciton and its relaxation to intermolecular $^1(\sigma-\pi^*)^{CT}$ charge transfer state.

## Conclusions

Synthesis of unsymmetrical polysilanes of the composition $-[R^1(Me)Si]_n-$ (**1**−**3**), $-[R^2(Me)Si]_n-$ (**4**−**6**), and $-[R^2(Ph)Si]_n-$ (**7**−**9**), bearing sila-substituted alkyl chains ($R^1$: $(CH_2)_3Si\equiv$; $R^2$: $(CH_2)_2Si\equiv$), has been achieved using Wurtz coupling reaction of the corresponding dichlorocarbosilane precursors. UV and photoluminescence (emission) spectral studies of polysilanes **1**−**6** reveal a marked dependence of $\sigma-\sigma^*$ electronic transition on the steric effect of silyl groups as well as alkyl chain length associated with pendant carbosilyl moiety. A detailed examination of UV and PL (emission and excitation) spectra of phenyl-substituted polysilanes **7**−**9** indicates that the origin of photoluminescent band in the visible region (VPL) can result from the $^1(\sigma-\pi^*)^{CT}$ charge-transfer state, although the contribution of branching defects in the backbone has not been completely ruled out. These polysilanes are interesting candidates to explore the functional group chemistry since silicon atoms associated with backbone as well as pendant carbosilyl chain can be utilized for chemical modification. This aspect is currently being investigated.

## Experimental Section

**General Comments.** All operations were carried out using standard Schlenk line techniques under a dry nitrogen atmosphere. Solvents were freshly distilled under inert atmosphere over sodium benzophenone (tetrahydrofuran, toluene) or magnesium (alcohols) before use. Glasswares were dried in an oven at 100−120 °C and further flame-dried under vacuum prior to use. Dichloromethylvinylsilane and allyldichloromethylsilane (Aldrich) were freshly distilled over magnesium. Karstedt's catalyst (platinum(0)−1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex), triethylsilane, phenyldimethylsilane, and diphenylmethylsilane (Aldrich) were used as received. Literature method was used to prepare $PhVinSiCl_2$.[20]

Infrared spectra were obtained as thin films on KBr pellets on a Nicolet FT-IR (Protégé) spectrophotometer. UV and photoluminescence spectra were recorded on a Perkin-Elmer (Lambada Bio 20) spectrophotometer and a Hitachi F-850 spectrofluorometer, respectively. Molecular weights of the polysilanes were estimated using a Waters 510 liquid chromatograph equipped with a Varian 400 refractive index detector and a Waters Styragel HR3 and HR4 column in series. The chromatograph was calibrated with polystyrene standards, and THF was used as eluent. $^1H$, $^{13}C\{^1H\}$, and $^{29}Si\{^1H\}$ NMR spectra were recorded in $CDCl_3$ on a Bruker spectrospin DPX 300 MHz instrument at frequency 300, 75.5, and 59.6 MHz, respectively, and chemical shifts are quoted relative to $Me_4Si$. $^{13}C\{^1H\}$ NMR spectra in DEPT-135 mode were obtained using a standard pulse sequence with $J$ modulation time 3.7 ms and 2 s delay time. HSQC ($^1H-^{13}C$) spectra were recorded using a standard pulse sequence with a relaxation delay of 2 s for each of the $512t_1$ experiments. Deconvolution was done using the peak fitting module of X Win NMR 1.3 by a Bruker spectrospin. Thermogravimetric analysis of polysilanes **1**−**9** was carried out in a $N_2$ atmosphere between 30 and 800 °C at a heating rate of 10 °C/min on a Perkin-Elmer thermal analysis system.

**Synthesis of the Carbosilane Precursors 1a**−**9a**. These carbosilanes were prepared by following the hydrosilylation approach.[21] To a stirred solution of allyldichloromethylsilane (11.71 g, 11 mL, 75.5 mmol) containing a catalytic amount of Karstedt's catalyst ($10^{-7}$ Pt/mol of silane), triethyl/phenyldimethyl/diphenylmethylsilane (75 mmol) was added dropwise at room temperature. Though the reaction mixture turned pale yellow after a few milliliters of hydrosilane was added, no induction period was observed during the complete addition. The reaction mixture was heated at 100 °C for 12 h, and the product obtained in each case was fractionally distilled to obtain the corresponding carbosilanes **1a**−**3a.** The carbosilanes **4a**−**6a** and **7a**−**9a** are obtained by following a similar procedure by reacting equimolar quantities of dichloromethylvinylsilane or dichlorophenylvinylsilane with the corresponding hydrosilanes. These carbosilanes are hitherto unknown and have been characterized by IR and multinuclear NMR studies. The relevant spectroscopic data are presented below. For assigning the NMR spectral data, the methylene group attached to the $SiCl_2$ moiety is represented with the notation α-, and subsequent groups are designated with $\beta$- and $\gamma$-notations.

**$Et_3SiCH_2CH_2CH_2SiMeCl_2$ (1a)** (bp 104−106 °C/5 mmHg, yield 60%). $^1H$ NMR: $\delta$ 1.52−1.41 (m, 2H, $\beta$-$CH_2$), 1.17−1.11 (m, 2H, α-$CH_2$), 0.86 (t, $^3J_{H-H} = 7.6$ Hz, 9H, $CH_3$−Et), 0.70 (s, 3H, Si$Me$Cl$_2$), 0.59−0.53 (m, 2H, $\gamma$-$CH_2$), 0.45 (q, $^3J_{H-H} = 7.9$ Hz, 6H, $CH_2$−Et). $^{13}C\{^1H\}$ DEPT-135 NMR: $\delta$ 26.31 ($\beta$-$CH_2$), 17.50 (α-$CH_2$), 15.31 ($\gamma$-$CH_2$), 7.65 ($CH_3$−Et), 5.63 (Si$Me$Cl$_2$), 3.45 ($CH_2$−Et). $^{29}Si\{^1H\}$ NMR: $\delta$ 7.17 ($Et_3Si$), 32.69 ($SiMeCl_2$).

**$PhMe_2SiCH_2CH_2CH_2SiMeCl_2$ (2a)** (bp 140−142 °C/5 mmHg, yield 83%). $^1H$ NMR: $\delta$ 7.41−7.27 (m, 5H, Si$Ph$), 1.49−

1.43 (m, 2H, β-CH$_2$), 1.14−1.06 (m, 2H, α-CH$_2$), 0.82−0.76 (m, 2H, γ-CH$_2$), 0.65 (s, 3H, SiMeCl$_2$), 0.20 (s, 6H, PhMe$_2$Si). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 134.15, 129.34, 128.59 (SiPh), 26.36 (β-CH$_2$), 19.12 (α-CH$_2$), 17.61 (γ-CH$_2$), 5.68 (SiMeCl$_2$), −3.48 (PhMe$_2$Si). $^{29}$Si{$^{1}$H} NMR: δ −2.73 (PhMe$_2$Si), 32.80 (SiMeCl$_2$).

**Ph$_2$MeSiCH$_2$CH$_2$CH$_2$SiMeCl$_2$ (3a)** (bp 160−165 °C/5 mmHg, yield 75%). $^{1}$H NMR: δ 7.61−7.40 (m, 10H, SiPh), 1.79−1.62 (m, 2H, β-CH$_2$), 1.31−1.24 (m, 4H, α- and γ-CH$_2$), 0.77 (s, 3H, SiMeCl$_2$), 0.65 (s, 3H, Ph$_2$MeSi). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 134.75, 129.39, 128.23 (SiPh), 25.97 (β-CH$_2$), 17.95 (α-CH$_2$), 17.61 (γ-CH$_2$), 5.70 (SiMeCl$_2$), −4.10 (Ph$_2$MeSi). $^{29}$Si{$^{1}$H} NMR: δ −6.92 (Ph$_2$MeSi), 32.79 (SiMeCl$_2$).

**Et$_3$SiXSiMeCl$_2$ (4a) [X = CH$_2$CH$_2$; CHCH$_3$]** (bp 95−100 °C/5 mmHg, yield 85%; product obtained as isomeric mixture in the ratio 92:8%). $^{1}$H NMR: δ 1.24 (d, CH−CH$_3$), 1.03−0.94 (m, CH$_3$−Et + α-CH$_2$ + SiMeCl$_2$), 0.66−0.52 (m, β-CH$_2$ + CH$_2$−Et), 0.84 (s, SiMeCl$_2$), 0.40 (m, Si−CHCH$_3$). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 15.68 (CH−CH$_3$), 14.69 (α-CH$_2$), 13.43 (β-CH$_2$), 7.58 (C−CH$_3$), 7.52 (CH$_3$−Et), 4.38, 4.67 (SiMeCl$_2$), 2.91, 2.27 (CH$_2$−Et). $^{29}$Si{$^{1}$H} NMR: δ 8.84, 7.88 (Et$_3$Si), 33.15, 32.58 (SiMeCl$_2$).

**PhMe$_2$SiXSiMeCl$_2$ (5a) [X = CH$_2$CH$_2$ ; CHCH$_3$]** (bp 95−97 °C/5 mmHg, yield 75%, product obtained as isomeric mixture in the ratio 93:7%). $^{1}$H NMR: δ 7.49−7.33 (m, SiPh), 1.19 (d, CHCH$_3$), 1.00−0.95 (m, α-CH$_2$), 0.82−0.78 (m, β-CH$_2$), 0.71, 0.64 (s, SiMeCl$_2$), 0.28, 0.22 (s, PhMe$_2$Si), 0.13 (m, CHCH$_3$).$^{13}$C{$^{1}$H} DEPT-135 NMR: δ 134.32, 129.87, 128.65 (Si−Ph), 15.32 (α-CH$_2$), 14.27 (CH−CH$_3$), 7.51 (β-CH$_2$), 6.69 (C−CH$_3$), 5.12, 4.97 (SiMeCl$_2$), −2.51, −2.86 (PhMe$_2$Si). $^{29}$Si{$^{1}$H} NMR: δ −0.76, −1.20 (PhMe$_2$Si), 33.64, 32.33 (SiMeCl$_2$).

Ph$_2$MeSiCH$_2$CH$_2$SiMeCl$_2$ (6a) (bp 140−145 °C/5 mmHg, yield 70%). $^{1}$H NMR: δ 7.57−7.28 (m, 10H, SiPh), 1.24−1.15 (m, 2H, α-CH$_2$), 1.12−1.03 (m, 2H, β-CH$_2$), 0.67 (s, 3H, SiMeCl$_2$), 0.49 (s, 3H, Ph$_2$MeSi). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 134.63, 129.61, 128.65 (Si−Ph), 14.72 (α-CH$_2$), 5.61 (β-CH$_2$), 4.57 (SiMeCl$_2$), −4.78 (Ph$_2$MeSi). $^{29}$Si{$^{1}$H} NMR: δ −5.35 (Ph$_2$MeSi), 33.56 (SiMeCl$_2$).

**Et$_3$SiCH$_2$CH$_2$SiPhCl$_2$ (7a)** (bp 145−147 °C/5 mmHg, yield 53%). $^{1}$H NMR: δ 7.77−7.49 (m, 5H, SiPh), 1.28−1.22 (m, 2H, α-CH$_2$), 0.98−0.93 (t, $^{3}J_{H-H}$ = 7.7 Hz, 9H, CH$_3$-Et), 0.72−0.66 (m, 2H, β-CH$_2$), 0.61−0.53 (q, $^{3}J_{H-H}$ = 7.3 Hz, 6H, CH$_2$−Et). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 133.70, 131.73, 128.52 (Si-Ph), 13.86 (α-CH$_2$), 7.50 (CH$_3$-Et), 3.04 (CH$_2$−Et), 2.42 (β-CH$_2$). $^{29}$Si{$^{1}$H} NMR: δ 9.73 (Et$_3$Si), 20.21 (SiPhCl$_2$).

**PhMe$_2$SiCH$_2$CH$_2$SiPhCl$_2$ (8a)** (bp 176−180 °C/5 mmHg, yield 67%). $^{1}$H NMR: δ 7.73−7.39 (m, 10H, SiPh), 1.29−1.23 (m, 2H, α-CH$_2$), 0.94−0.89 (m, 2H, β-CH$_2$), 0.33 (s, 6H, PhMe$_2$Si). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 133.81, 133.69, 131.75, 129.34, 128.51, 128.10 (SiPh), 13.86 (α-CH$_2$), 7.06 (β-CH$_2$), −3.31 (PhMe$_2$Si). $^{29}$Si{$^{1}$H} NMR: δ 0.11 (PhMe$_2$Si), 20.34 (SiPhCl$_2$).

**Ph$_2$MeSiCH$_2$CH$_2$SiPhCl$_2$ (9a)** (bp 190−195 °C/5 mmHg, yield 70%). $^{1}$H NMR: δ 7.61−7.29 (m, 15H, SiPh), 1.21−1.10 (m, 4H, α- and β-CH$_2$), 0.49 (s, 3H, Ph$_2$MeSi). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 134.23, 133.16, 131.42, 130.03, 128.58, 128.16 (Si−Ph), 13.90 (α-CH$_2$), 7.10 (β-CH$_2$), −4.03 (Ph$_2$MeSi). $^{29}$Si{$^{1}$H} NMR: δ −6.94 (Ph$_2$MeSi), 20.32 (SiPhCl$_2$).

**Preparation of Polysilanes 1−9.** In a typical procedure, freshly weighed sodium (1.00 g, 43.4 mmol) was transformed to a fine dispersion in refluxing toluene under a dry nitrogen atmosphere, and the dichlorocarbosilane precursors **1a**−**9a** (19.0 mmol) were added separately into it with the help of a hypodermic syringe. The reaction mixture in each case 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 of from the filtrate to afford a crude polymer in each case. The corresponding high molecular weight polysilanes were obtained as viscous gum (**1**−**6**) or solid (**7**−**9**) by careful centrifugation of the crude products using a toluene/2-propanol mixture.

**−[Et$_3$SiCH$_2$CH$_2$CH$_2$SiMe]$_n$− (1).** $^{1}$H NMR: δ 1.31 (br, 2H, β-CH$_2$), 0.85 (t, $^{3}J_{H-H}$ = 7.2 Hz, 11H, CH$_3$−Et + α-CH$_2$), 0.53 (br, 2H, γ-CH$_2$), 0.42 (q, $^{3}J_{H-H}$ = 7.7 Hz, 6H, CH$_2$−Et), 0.18 (s, 3H, SiMe).$^{13}$C{$^{1}$H} DEPT-135 NMR: δ 21.98 (β-CH$_2$), 20.83 (α-CH$_2$), 17.71 (γ-CH$_2$), 7.90 (CH$_3$−Et), 3.88 (CH$_2$−Et), 3.83 (SiMe). $^{29}$Si{$^{1}$H} NMR: δ 6.56 (s, Et$_3$Si), −26.88 (br, SiMe).

**−[PhMe$_2$SiCH$_2$CH$_2$CH$_2$SiMe]$_n$− (2).** $^{1}$H NMR: δ 7.34, 7.17 (br, 5H, SiPh), 1.25 (br, 2H, β-CH$_2$), 0.70 (br, 4H, α- and γ-CH$_2$), 0.13 (s, 6H, PhMe$_2$Si), 0.03 (s, 3H, SiMe). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 134.94, 129.27, 128.22 (SiPh), 21.84 (β- and γ-CH$_2$), 20.16 (α-CH$_2$), −2.62 (PhMe$_2$Si), −3.62, −3.74, −3.92 (SiMe). $^{29}$Si{$^{1}$H} NMR: δ −1.18 (s, PhMe$_2$Si), −26.31 (br, SiMe).

**−[Ph$_2$MeSiCH$_2$CH$_2$CH$_2$SiMe]$_n$− (3).** $^{1}$H NMR: δ 7.47, 7.26 (br, 10H, SiPh), 1.40 (br, 2H, β-CH$_2$), 1.10 (br, 2H, γ-CH$_2$), 0.82 (br, 2H, α-CH$_2$), 0.53 (s, 3H, Ph$_2$MeSi), 0.02 (br, 3H, SiMe). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 134.57, 129.32, 128.03 (SiPh), 21.66 (β-CH$_2$), 19.97 (α- and γ-CH$_2$), −3.96 (Ph$_2$MeSi), −4.12 (SiMe). $^{29}$Si{$^{1}$H} NMR: δ −7.93 (s, Ph$_2$MeSi), −25.89 (br, SiMe).

**−[Et$_3$SiXSiMe]$_n$− (4) [X = CH$_2$CH$_2$; CHCH$_3$].** The CHCH$_3$ group has eluded detection in $^{1}$H and $^{13}$C{$^{1}$H } NMR spectra. However, its presence in the polymer is reminiscent of the $^{29}$Si{$^{1}$H} NMR studies. $^{1}$H NMR: δ 0.95 (t, $^{3}J_{H-H}$ = 7.7 Hz, 9H, CH$_3$-Et), 0.42−0.57 (br, 10H, α- and β-CH$_2$ + CH$_2$−Et), 0.06 (s, 3H, Si−Me). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 9.91 (α-CH$_2$), 8.98 (β-CH$_2$), 7.63 (CH$_3$−Et), 4.24 (CH$_2$−Et), −4.85 (Si−Me). $^{29}$Si{$^{1}$H} NMR: δ 8.48, 7.84 (s, Et$_3$Si), −27.82 (br, Si−Me).

**−[PhMe$_2$SiXSi]$_n$− (5) [X = CH$_2$CH$_2$; CHCH$_3$].** The CHCH$_3$ group has eluded detection in $^{1}$H and $^{13}$C{$^{1}$H} NMR spectra. However, its presence in the polymer is reminiscent of the $^{29}$Si{$^{1}$H} NMR studies. $^{1}$H NMR: δ 7.49, 7.28 (br, 5H, SiPh), 0.85 (br, 4H, α- and β-CH$_2$), 0.26 (s, 6H, PhMe$_2$Si), 0.03 (s, 3H, SiMe). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 134.23, 128.68, 127.46 (Si−Ph), 10.48 (β-CH$_2$), 9.23 (α-CH$_2$), 2.95 (PhMe$_2$Si), −5.12 (Si−Me). $^{29}$Si{$^{1}$H} NMR: δ 0.42, −1.32 (s, PhMe$_2$Si), −27.75 (br, SiMe).

**−[Ph$_2$MeSiCH$_2$CH$_2$SiMe]$_n$− (6).** $^{1}$H NMR: δ 7.39, 7.21 (br, 10H, SiPh), 0.88 (br, 2H, β-CH$_2$), 0.72 (br, 2H, α-CH$_2$), 0.43 (s, 3H, Ph$_2$MeSi), 0.06 (br, 3H, SiMe). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 134.29, 128.95, 127.63 (Si−Ph), 9.66 (β-CH$_2$), 6.94 (α-CH$_2$), −4.72 (Ph$_2$MeSi), −5.06 (SiMe). $^{29}$Si{$^{1}$H} NMR: δ −6.53 (s, Ph$_2$MeSi), −27.65 (br, SiMe).

**−[Et$_3$SiCH$_2$CH$_2$SiPh]$_n$− (7).** $^{1}$H NMR: δ 7.19 (br, 5H, Si−Ph), 0.96−0.62 (br, 10H, α- and β-CH$_2$ + CH$_2$−Et), 0.53 (br, 9H, CH$_3$−Et). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 135.37, 127.31 (br, Si−Ph), 7.94 (CH$_3$−Et), 2.51 (α- and β-CH$_2$ + CH$_2$−Et). $^{29}$Si{$^{1}$H} NMR: δ 8.68 (s, Et$_3$Si), −31.36 (br, SiPh).

**−[PhMe$_2$SiCH$_2$CH$_2$SiPh]$_n$− (8).** $^{1}$H NMR: δ 7.50 (br, 10H, SiPh), 0.78 (br, 4H, α- and β-CH$_2$), 0.32 (s, 6H PhMe$_2$Si). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 136.22, 134.16, 129.19, 128.14 (SiPh), 13.64 (β-CH$_2$), 7.82 (α-CH$_2$), −3.14 (PhMe$_2$Si). $^{29}$Si{$^{1}$H} NMR: δ −1.48 (s, PhMe$_2$Si), −30.72 (br, SiPh).

**−[Ph$_2$MeSiCH$_2$CH$_2$SiPh]$_n$− (9).** $^{1}$H NMR: δ 7.55 (br, 15H, SiPh), 0.75 (br, 4H, α- and β-CH$_2$), 0.40 (s, 3H, Ph$_2$MeSi). $^{13}$C{$^{1}$H} DEPT-135 NMR: δ 135.48, 129.91, 127.46 (Si−Ph), 13.73 (β-CH$_2$), 7.02 (α-CH$_2$), −3.67 (Ph$_2$MeSi). $^{29}$Si{$^{1}$H} NMR: δ −5.63 (s, Ph$_2$MeSi), −31.71 (br, SiPh).

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