# SYNTHESIS, CHARACTERIZATION AND REACTIVITY STUDIES OF ASYMMETRICALLY SUBSTITUTED POLYSILANES WITH APPENDED CARBOSILYL GROUPS

BY

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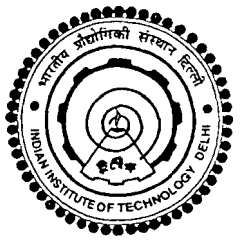
**Department of Chemistry**

Submitted

in fulfillment of the requirements of the degree of

**DOCTOR OF PHILOSOPHY**

**to the**




**INDIAN INSTITUTE OF TECHNOLOGY, DELHI**

**NOVEMBER, 2006**

*Dedicated to my parents*

## CERTIFICATE

This is to certify that the thesis entitled, "***Synthesis, characterization and reactivity studies of asymmetrically substituted polysilanes with appended carbosilyl groups***", being submitted by Ms. Arti Joshi to the Indian Institute of Technology, Delhi for the award of degree of Doctor of Philosophy is a bonafide work carried out by her. Ms. Arti Joshi has worked under my guidance and supervision and fulfilled all the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard. The results embodied in this thesis have not been submitted, in part or full to any other University or Institute for award of any degree or diploma.

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Arti

**Arti Joshi**

## ABSTRACT

The work embodied in the present thesis deals with a systematic study on the synthesis and characterization of hitherto unknown polysilanes, $-[RR'_2Si(CH_2)_xSiR^1]_n-$ (x = 2 or 3, $R^1$ = Me, Ph, H or carbosilyl) as well as copolysilanes, $\{[RR'_2Si(CH_2)_2SiMe]_x[PhR^1Si]_{1-x}\}_n$ ($R^1$ = Ph, Me; R, R′ = Me, Et or Ph) bearing carbosilyl side chains as pendant substituents. These studies assume significance in view of the following reasons. The structural characteristics of silaalkanes are known to differ from those of the corresponding *n*-alkanes. Thus, it has been envisioned that polysilanes associated with appended carbosilyl groups may differ in their electronic properties associated with $\sigma$-$\sigma^*$ transition in comparison to those of poly(dialkylsilane)s. This concept has been studied in a variety of newly synthesized polysilanes and a detail account of the results is described in chapters 3-6 of the present dissertation. The contents of each chapter are summarized as follows:

**Chapter 3 – Synthesis and characterization of carbosilane monomers**

In this chapter, synthesis and characterization of a number of carbosilane monomers of the composition, $RR'_2Si(CH_2)_xSiMeCl_2$ are described. These carbosilanes have been subsequently used for the synthesis of the desired polysilanes by Wurtz coupling method. Thus, hydrosilylation of a triorganosilane with dichloromethylvinyl/ allyldichloromethylsilane in presence of Karstedt's catalyst affords the corresponding carbosilanes (**1-6**).

$$RR'_2SiH + CH_2{=}CHSiMeCl_2 \xrightarrow{\text{Karstedt's catalyst}} RR'_2SiCH_2CH_2SiMeCl_2$$

**(1-3)**

R = R' = Et (**1**); R = Ph; R' = Me (**2**); R = Me; R' = Ph (**3**)

$$RR'_2SiH + CH_2=CHCH_2SiMeCl_2 \xrightarrow{\text{Karstedt's catalyst}} RR'_2SiCH_2CH_2CH_2SiMeCl_2$$

(4-6)

R = R' = Et (4); R = Ph; R' = Me (5); R = Me; R' = Ph (6)

Analogous reaction of triphenylsilane with dichloromethylvinylsilane under Pt-catalyzed conditions gives rise to the carbosilane, $Ph_3Si(CH_2)_2SiMeCl_2$ (7) as the major product along with minor amounts of 1,1,1,4,4,4-hexaphenyl-1,4-disilabutane (8). The formation of compound 8 is believed to arise from ligand-exchange phenomenon involving vinyl/H groups in the precursors under Pt-catalyzed conditions.

$$Ph_3SiH + CH_2=CHSiMeCl_2 \rightleftharpoons CH_2=CHSiPh_3 + HSiMeCl_2$$

All the carbosilanes obtained above are colorless, distillable liquids with the exception of 7 and 8 which are white solids. The identity of these compounds has been established by IR and multinuclear ($^1H$, $^{13}C$, $^{29}Si$) NMR spectral studies. In general, the NMR spectral data are in accord with the proposed composition, although minor amounts of the other isomer $RR'_2SiCH(CH_3)SiMeCl_2$ (7-8 %) have also been detected in the carbosilane 1 and 2. In particular, $^{29}Si$ NMR data has been quite useful in the detection of these isomers (table 1).

X-ray crystal structures of the carbosilanes 7 and 8 have been investigated to establish the identity of these carbosilanes. The compound $Ph_3Si(CH_2)_2SiMeCl_2$ (7) crystallizes in the space group $P2_1/c$ [monoclinic, a = 7.6677(9) Å, b = 11.5230(13) Å, c = 23.061(3) Å, $\alpha$ = 90°, $\beta$ = 91.200(1)°, $\gamma$ = 90°, Z = 4]. The molecule adopts a trans-planar conformation of Si-C-C-Si unit (torsional angle -178.4(1)°). The Si-C-C angles subtended by the methylene groups [117.0(1); 116.7(1)°] are found to be the largest known so far, as might

**Table 1: $^{29}Si\{^1H\}$ NMR spectral data (δ, ppm) of carbosilanes (1-8)**

| S.No | Carbosilane | $RR'_2Si$ | $SiMeCl_2$ |
|---|---|---|---|
| 1 | $Et_3Si(CH_2)_2SiMeCl_2$ | 8.84, 7.88 | 33.15, 32.58 |
| 2 | $PhMe_2Si(CH_2)_2SiMeCl_2$ | -0.76, -1.20 | 33.64, 32.33 |
| 3 | $Ph_2MeSi(CH_2)_2SiMeCl_2$ | -5.35 | 33.56 |
| 4 | $Et_3Si(CH_2)_3SiMeCl_2$ | 7.17 | 32.69 |
| 5 | $PhMe_2Si(CH_2)_3SiMeCl_2$ | -2.73 | 32.80 |
| 6 | $Ph_2MeSi(CH_2)_3SiMeCl_2$ | -6.92 | 32.79 |
| 7 | $Ph_3Si(CH_2)_2SiMeCl_2$ | -8.38 | 32.68 |
| 8 | $Ph_3Si(CH_2)_2SiPh_3$ | -8.50 | |

be expected in sterically congested system. The influence of bulky $Ph_3Si$ group is also reminiscent in the observed Si1-C19 bond length, 1.899(2) Å which lies at the upper end of the normal range accepted for Si-C bond (1.86-1.91 Å). The molecules self assemble in 3-D supramolecular motifs via C-H---Cl and C-H---π interactions (figure 1).

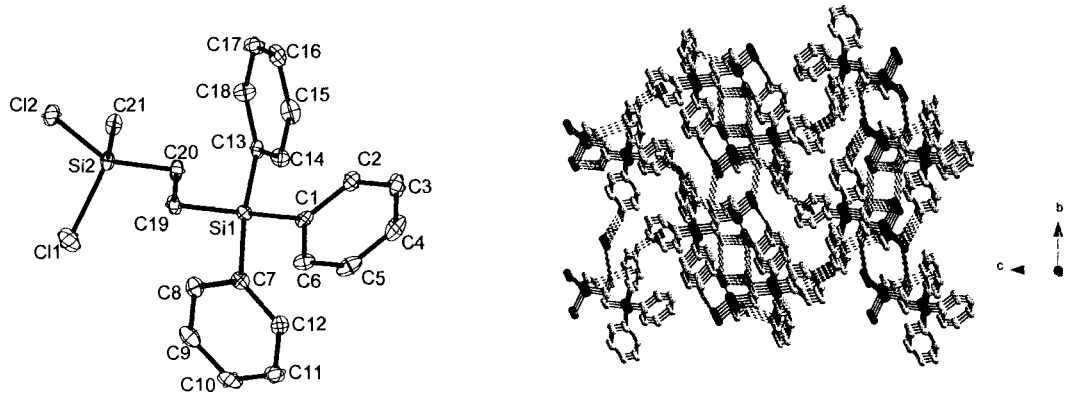



**Figure 1: (a) ORTEP view of $Ph_3SiCH_2CH_2SiMeCl_2$ (7) (b) 3-D supramolecular assembly showing hydrogen bonding interactions: C-H····Cl (red dotted lines) and C-H····π (blue dotted lines)**

The compound $Ph_3SiCH_2CH_2SiPh_3$ (**8**) crystallizes in the space group $P\bar{1}$ [triclinic, a =7.8468(9) Å, b = 9.4743(10) Å, c = 21.464(2) Å, $\alpha$ = 96.460(2)°, $\beta$ = 93.190(2)°, $\gamma$ = 111.239(2)°, Z = 2]. The molecular structure comprises of two independent molecules in the unit cell of which only one is shown in figure 2. The structure of each molecule lies on a crystallographic inversion center and adopts a trans-planar conformation of the Si-C-C-Si unit with nearly identical metrical parameters [Si1-C19 1.881(5) Å, Si2-C38 1.879(4) Å, C19-C19 1.538(9) Å, C38-C38 1.537(8) Å, C19-C19-Si1 116.5(4)°, C38-C38-Si2 117.0(4)°]. However, subtle structural differences in the relative orientations of various phenyl rings are evident from the dihedral angles C-Si-C*ipso*-C*ortho*, the largest observed deviation being 3.9°. These results are in conformity with the superposition plot as shown in figure 2. The molecule adopts a 3-D supramolecular assembly by virtue of extensive CH····$\pi$ interactions between the arene rings.

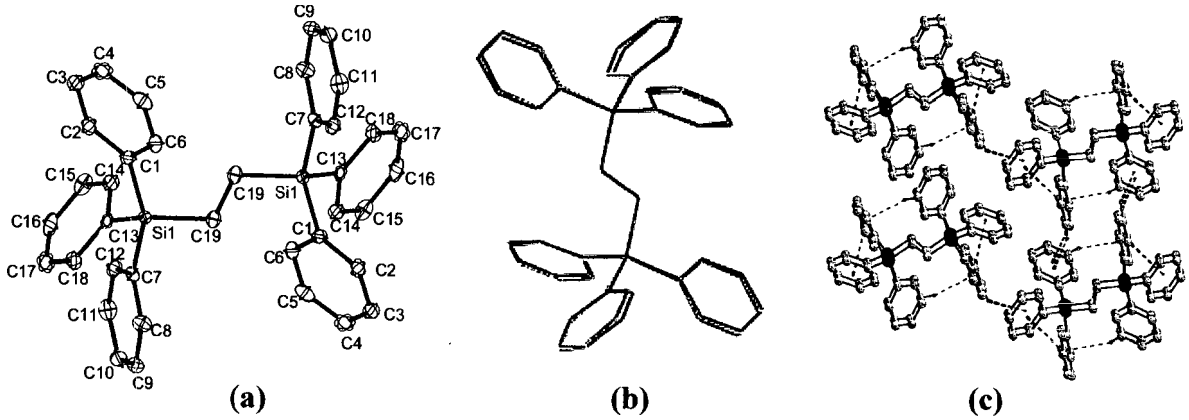
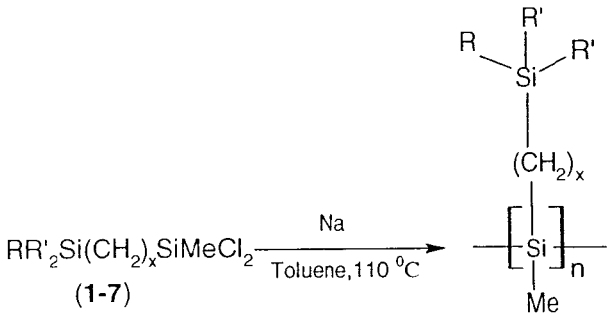



**Figure 2: (a) ORTEP view of $Ph_3SiCH_2CH_2SiPh_3$ (8) (b) Superposition plot of the independent molecules (c) 3-D view showing C-H····$\pi$ interactions (red dotted lines)**

**Chapter 4- Synthesis and characterization of polysilanes and copolysilanes bearing methyl- and carbosilyl groups.**

As shown in scheme 1, carbosilanes, $RR'_2Si(CH_2)_xSiMeCl_2$ upon reaction with sodium metal dispersion in toluene afford the corresponding linear high molecular weight polysilanes (yield 5-12%). All the polysilanes obtained herein are viscous gums except **7a** which is obtained as a solid. These are soluble in common organic solvents such as toluene, THF, chloroform, dichloromethane, benzene etc. Thermogravimetric analysis (TGA) reveals that these polymers are stable upto 370-400 °C. However, continuos weight loss is observed upto 500 °C leaving a residual yield of 7-10 %.




x = 2; R = R' = Et (**1a**); R = Ph, R' =Me (**2a**); R = Me, R' = Ph (**3a**)

x = 3; R = R' = Et (**4a**); R = Ph, R' = Me (**5a**); R = Me, R' = Ph (**6a**)

x = 2; R = R' = Ph (**7a**)

**Scheme 1**

GPC analysis of these polysilanes exhibit a monomodal molecular weight distribution with Mw ranging between (31-237)$\times 10^3$ and polydispersity PDI = 1.55-1.82. The identity of carbosilyl side chains has been established by $^1H$ and $^{13}C$ NMR spectroscopy. $^1H$ NMR spectrum of each polymer 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. The unresolved $^{1}H$ and $^{13}C\{^{1}H\}$ resonances of methylene groups may accordingly be attributed to short spin-spin relaxation time of these nuclei. A detailed analysis of the overlapping resonances in the $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra have been made by the ($^{1}H$-$^{13}C$) HSQC NMR spectroscopy. A common feature in the $^{29}Si\{^{1}H\}$ NMR spectra of the polysilanes **3a-7a** is the appearance of a sharp singlet at δ 6.56 to -8.40 and a broad featureless signal at δ -25.89 to -27.82. The former chemical shift value is ascribed to the carbosilyl side groups and the later to silicon backbone. For polysilanes **1a** and **2a**, two distinct $^{29}Si\{^{1}H\}$ NMR signals appear in the carbosilyl region at δ 8.48, 7.84 and 0.42, -1.32 respectively and are corroborated with the presence of both α (minor) and β (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.

A detailed microstructure analysis of the polymer **5a** (figure 3) has been performed by deconvolution of the $^{13}C\{^{1}H\}$ NMR resonances at δ -3.62, -3.74, -3.92 due to Si-Me (backbone). The signal at δ -3.62 is tentatively assigned to rr stereo domain while the high field resonances at δ -3.74 and -3.92 are subscribed to rm/ mr and mm stereodomains respectively. On the basis of deconvolution studies, the signal intensity of each chemical shift region is deduced and intensity ratio of the triad domain (rr: rm/ mr: mm) has been evaluated as 0.44: 0.45: 0.10. A good agreement between calculated values and those predicted by Bernoullian statistics (0.46: 0.43: 0.10) is observed with Pm = 0.32 and Pr = 0.68. These results suggest that the polysilane adopts predominantly atactic configuration with a syndiotactic bias. Unfortunately, configurational analysis for polysilanes **3a**, **4a**, **6a** and **7a** 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 **1a** and **2a** are precluded due to the presence of α and β isomeric mixtures.

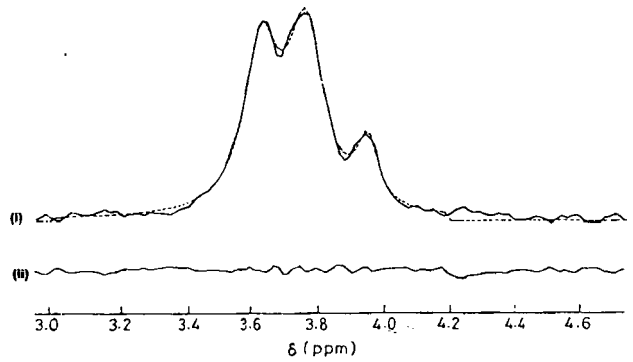



**Figure 3: Partial $^{13}C\{^1H\}$ NMR spectrum of -[$PhMe_2Si(CH_2)_3SiMe]_n$- (5a) depicting Si-*Me* (backbone) region (i) spectrum (solid line) and calculated spectrum (dotted line) (ii) difference between actual and calculated spectrum.**

UV absorption spectra of the polysilanes **1a-7a** reveal a strong absorption at $\lambda_{max}$: 296-317 nm in each case associated with $\sigma$-$\sigma^*$ electronic transition. As evident from figure 4, a discernable variation in the $\lambda_{max}$ and ε (molar absorptivity) values are observed which reflect the conformational sensitivity of silicon backbone towards the appended silyl moieties and $(CH_2)_x$ chain length. It has been observed that polysilanes (**4a-6a**) bearing longer $CH_2CH_2CH_2$ chains exhibit higher $\lambda_{max}$ and ε values ($\lambda_{max}$ = 303-317 nm with ε = 2800-5900 (Si repeat unit)$^{-1}$dm$^3$cm$^{-1}$) in comparison to polysilanes **1a-3a** and **7a** possessing $CH_2CH_2$ groups ($\lambda_{max}$ = 296-311 nm with ε = 1100-3000 (Si repeat unit)$^{-1}$dm$^3$cm$^{-1}$). In addition, the spectral behavior of these polysilanes shows a strong dependence on the nature of substitutents on the silicon atom of carbosilyl groups. For the polysilanes bearing appended sila-substituents such as $Et_3Si$ (**1a**), $PhMe_2Si$ (**2a**) $Ph_2MeSi$ (**3a**) and $Ph_3Si$ (**7a**) on the carbosilyl moiety, it

is observed that both $\lambda_{max}$ and $\varepsilon$ values increase with increase in stericity of the sila-substituents. The relative order of bathochromic shift follows the order $Et_3Si<PhMe_2Si\sim Ph_2MeSi<Ph_3Si$. A similar trend is observed for the polysilanes **4a-6a**. The higher values of absorption maxima and increased absorptivity in polysilanes **4a-6a** 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. These results along with PL (emission) spectral studies suggest that these polymers adopt a random coil conformation.

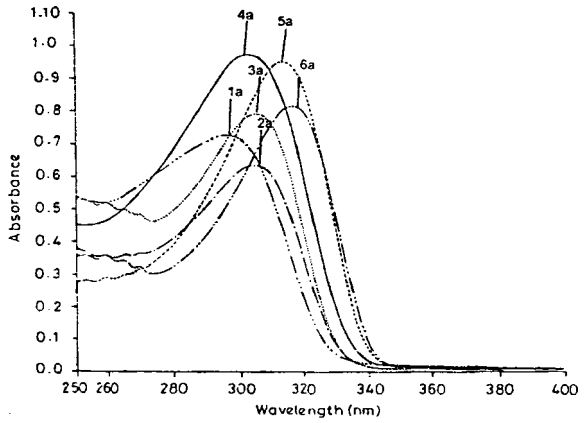
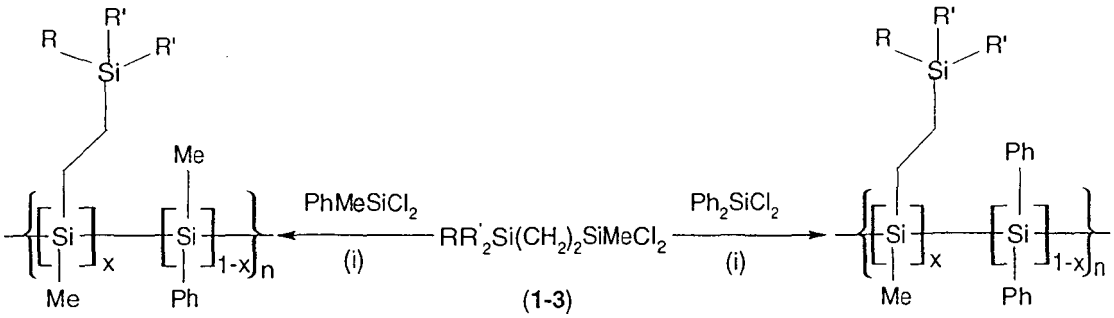



**Figure 4: UV spectra (THF, RT) of polysilanes (1a-6a)**

Synthesis of the copolymers, $\{[RR'_2Si(CH_2)_2SiMe]_x[PhR^1Si]_{1-x}\}_n$ has been achieved by co-condensation of the carbosilanes, $RR'_2Si(CH_2)_2SiMeCl_2$ (**1-3**) and $PhR^1SiCl_2$ ($R^1$ = Me or Ph) in 1:1 molar ratio using sodium dispersion in toluene (scheme 2).




Reaction conditions: (i) Na, toluene, 110 $^{0}$C, 4h

| Polysilane | R, R' | x:1-x |
|---|---|---|
| **1b, 1c** | Et, Et | 0.36:0.64, 0.34:0.66 |
| **2b, 2c** | Ph, Me | 0.5:0.5, 0.42:0.58 |
| **3b, 3c** | Me, Ph | 0.5:0.5, 0.48:0.52 |

**Scheme 2**

All the polysilanes obtained herein are white solids and are soluble in common organic solvents such as toluene, THF, chloroform, dichloromethane, benzene etc. An analysis of GPC data reveals Mw = (112-25)×$10^3$ and polydispersity (PDI) = 1.36-5.49. $^1$H and $^{13}$C{$^1$H} NMR spectra of these copolysilanes are in accord with the suggested composition. $^{29}$Si{$^1$H} NMR spectra of the copolymers **1b-3b** associated with -[RSiMe]- (R = carbosilyl) and –[PhMeSi]- units reveal major resonances in the chemical shift domain of δ 7.73 to -6.48, -27.26 to -28.10 and -39.24 to -41.25 which are ascribed to pendant carbosilyl group, -[RSiMe]- and –[PhMeSi]- units respectively (figure 5). A detailed analysis of the $^{29}$Si{$^1$H} NMR spectral data suggest that the polymer backbone in each case contains long runs of –[PhMeSi]- and -[RSiMe]- units. In this respect, these polymers can be regarded as "block copolymers". On the other hand, the copolysilanes **1c-3c** bearing -[$Ph_2$Si]- units, in general show a broad massif at δ -24.01 to -37.00 due to the silicon backbone thereby precluding the assignments associated with -[RSiMe]- and

-[$Ph_2Si$]- units. The broadness of these peaks indicates that many different environments exist in the polymer, both configurational and conformational. However, distinct $^{29}Si$ NMR signals due to side chain carbosilyl groups appear at their routine position.

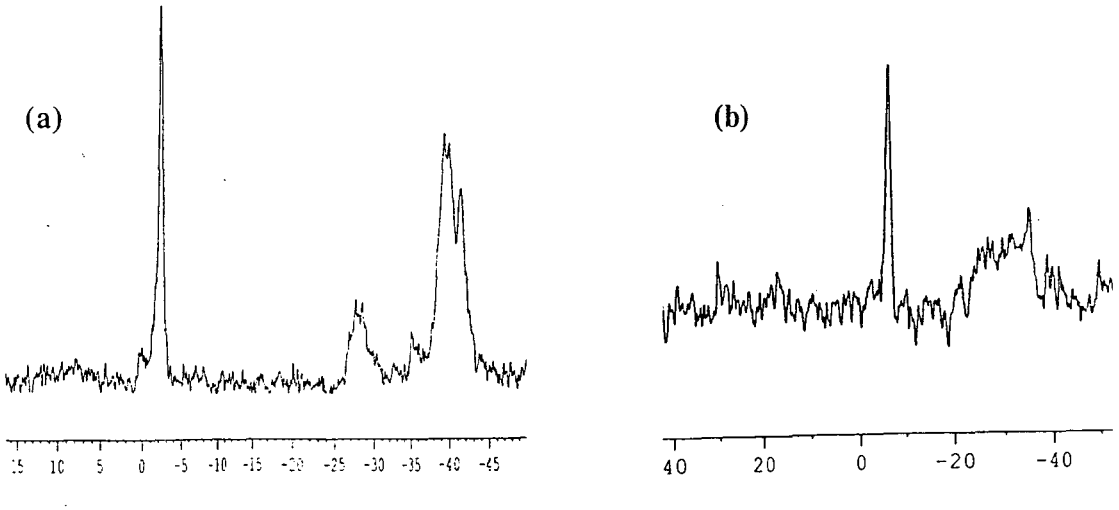



**Figure 5: $^{29}Si\{^1H\}$ NMR spectra of (a) $\{[PhMe_2Si(CH_2)_2SiMe]_x[PhMeSi]_{1-x}\}_n$ (2b) (b) $\{[Ph_2MeSi(CH_2)_2SiMe]_x[Ph_2Si]_{1-x}\}_n$ (3c)**

The UV spectra of the copolymers [RSiMe][$Ph_2Si$] (**1c-3c**) show an increased $\lambda_{max}$ values (321-352 nm) in comparison to those observed for the copolymers [RSiMe][PhMeSi] (**1b-3b**) ($\lambda_{max}$: 312-328 nm) bearing similar carbosilyl (R) side chains (figure 6). A plausible explanation for the observed variations in the electronic properties of these copolysilanes may come from a consideration of conformational features. It is believed that presence of two bulky geminal phenyl substituents in polysilanes **1c-3c** favor a more extended trans conformation in solution relative to polysilanes **1b-3b** and thus show a discernable bathochromic shift in the $\lambda_{max}$. In addition, the observed variations in the absorption maxima for copolymers (**1b-3b**) suggest that steric influence of the side chain

silyl substituents is significant in altering the electronic properties. A similar trend is observed in copolymers (**1c-3c**) as well.

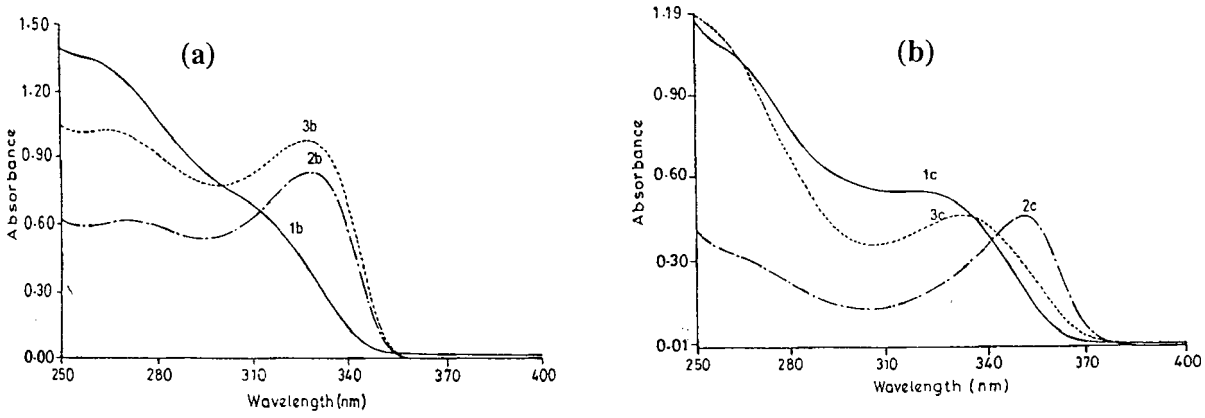



Figure 6: UV spectra (THF, RT) of (a) $\{[RR'_2Si(CH_2)_2SiMe]_x[PhMeSi]_{1-x}\}_n$ (1b-3b) (b) $\{[RR'_2Si(CH_2)_2SiMe]_x[Ph_2Si]_{1-x}\}_n$ (1c-3c)

**Chapter 5– Synthesis and characterization of polysilanes bearing phenyl- and carbosilyl side chains**

The synthesis of a few carbosilanes of the general formula $RR'_2SiCH_2CH_2SiPhCl_2$ (**9-12**) has been achieved by following the hydrosilylation method.

$$RR'_2SiH + CH_2{=}CHSiPhCl_2 \longrightarrow RR'_2SiCH_2CH_2SiPhCl_2$$

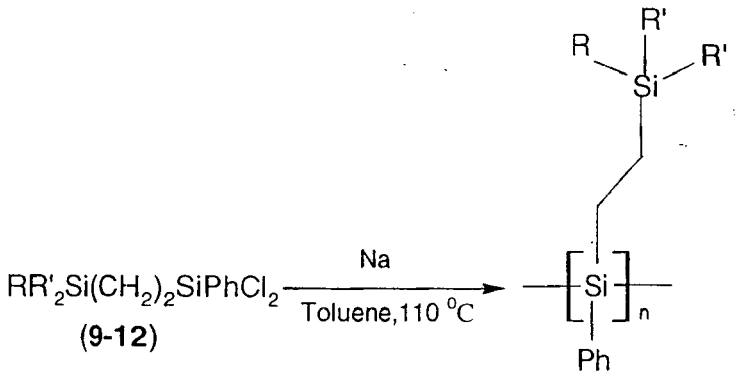
R = R' = Et (**9**); R = Ph; R' = Me (**10**); R = Me; R' = Ph (**11**)

$$Ph_3SiH + CH_2{=}CHSiPhCl_2 \longrightarrow \underset{(12)}{Ph_3SiCH_2CH_2SiPhCl_2} + \underset{(8)}{Ph_3SiCH_2CH_2SiPh_3}$$

Reaction conditions: Karstedt's catalyst, 100 $^0$C

All the carbosilanes are colorless, distillable liquids except **12** which is obtained as a viscous liquid. The identity of these compounds has been established by IR and multinuclear NMR ($^1$H, $^{13}$C, $^{29}$Si) spectroscopy.

The dichlorocarbosilanes, **9-12** have been subjected to Wurtz type condensation to afford the corresponding polysilanes **9a-12a** (scheme 3). These are obtained as white solids and are soluble in common organic solvents such as toluene, THF, chloroform, dichloromethane, benzene etc. GPC analysis reveal a monomodal molecular weight distribution in each case with Mw (3.4-2.3) $\times 10^3$ and PDI = 1.18-1.40.




(9a-12a)

R = R' = Et (**9a**); R = Ph, R' = Me (**10a**); R = Me, R' = Ph (**11a**); R = R' = Ph (**12a**)

**Scheme 3**

A notable feature in the IR spectra of **9a-12a** is the appearance of a weak intensity band at 2083-2090 $cm^{-1}$ due to νSiH end groups. This has been attributed to arise from abstraction of hydrogen from the solvent by silyl radicals. $^1H$ NMR spectrum of each polymer shows broad and featureless signals for the organic functional groups associated with the carbosilyl side chain and are devoid of J-coupling information. $^{13}C\{^1H\}$NMR spectra both in normal and DEPT-135 mode are quite informative and provide evidence for the phenyl and carbosilyl moieties attached to the polymer backbone. The $^{29}Si\{^1H\}$NMR spectra reveal a sharp singlet at δ 8.68 to -10.26 and a featureless signal at δ -30.72 to -33.16 corresponding to the appended carbosilyl group and silicon backbone respectively.

The UV spectra of the polysilanes, **9a-11a** typically shows two absorptions with $\lambda_{max}$ at 321-325 ($\sigma$-$\sigma^*$) and 262-265 nm ($\pi$-$\pi^*$) where as polysilane **12a** shows a complete disappearance of typical Si-Si backbone transition. The origin of disappearance of this electronic transition is not understood yet. It is however believed that the effect of bulky $Ph_3Si$- substituted carbosilyl side chain seems to alter the electronic behavior as a result of a significant change in the polymer backbone conformation. By analogy with the literature precedence, the polymer **12a** may be assumed to adopt a conformationally locked all-gauche form. This result may be qualitatively correlated with the observed $^{29}Si$ NMR chemical shift of backbone silicon framework which shows a perceptible upfield shift ($\delta$ -33.16 ppm) in comparison to those found in **9a-11a** ($\delta$ -30.72 to -31.71). A similar correlation between the $^{29}Si$ NMR and the backbone conformation has been reported for poly(di-*n*-butylsilane). An interesting feature of the photoluminescence (PL) emission spectra of these polysilanes is the appearance of a narrow band at 354-370 nm which tails in the visible region (VPL) with an edge at ca. 500 nm (figure 7). A detailed examination of PL (emission and exicitation) spectra indicates that origin of photoluminescent band in the visible region (VPL) can result from $^1(\sigma\text{-}\pi^*)^{CT}$ charge transfer state, although the contribution from the branching defects in the polymer backbone cannot be completely ruled out.

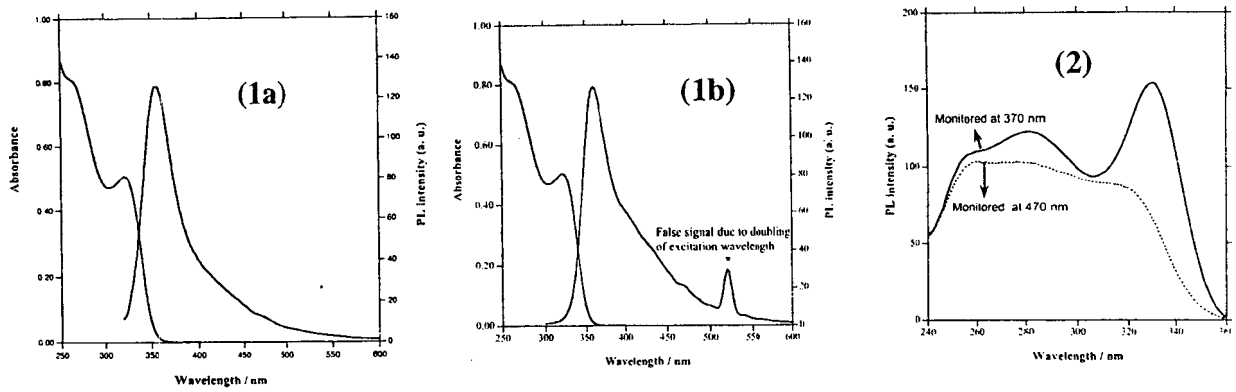



**Figure 7: (1) UV and PL (Emission spectra) (THF, RT) of $[PhMe_2SiCH_2CH_2SiPh]_n$- (10a) (a) excitation $\lambda_{max}$ = 315 nm (b) excitation $\lambda_{max}$ = 260 nm (2) Excitation spectra**

**Chapter 6- Synthesis of poly(hydrosilane)s, $-[R^1(H)Si]_n-$ ($R^1 = (CH_2)_3SiRR'_2$; R, R' = Me, Et or Ph) and their reactivity studies towards allyl/vinylsilanes.**

For the synthesis of the poly(hydrosilane)s, the desired carbosilane precursors (**13-15**) with terminal $SiH_3$ group are obtained by using hydrosilylation approach .

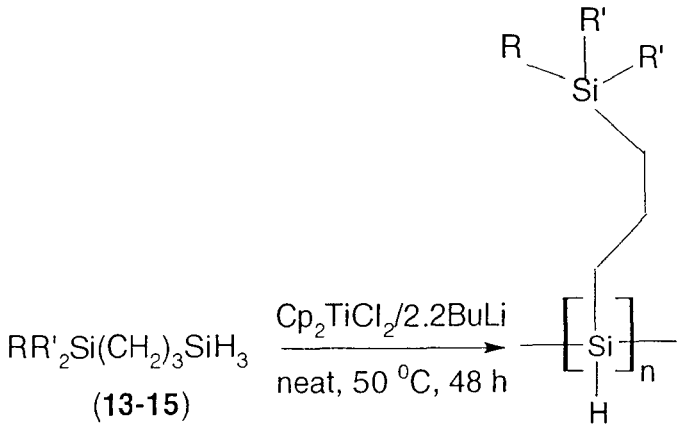
$$RR'_2SiH + CH_2{=}CHCH_2SiCl_3 \xrightarrow{\text{(i), (ii)}} RR'_2SiCH_2CH_2CH_2SiH_3$$

R = R' = Et (**13**);R = Ph; R' = Me (**14**); R = Me; R' = Ph (**15**)

Reaction conditions: (i) Karstedt's catalyst, 100 $^0$C (ii) $LiAlH_4$

All the carbosilanes obtained above are colorless, distillable liquids and identified by the characteristic $[M-H]^+$ ion in the EI-mass spectra. In the IR spectra, the primary $SiH_3$ group gives rise to characteristic absorptions at 2149-2148 (νSiH) and 924-923 ($\delta SiH_2$) $cm^{-1}$. Further evidence in support of the structure comes from $^{29}Si$ NMR spectra which identify $SiH_3$ groups at δ -56.46 to -63.97 (q, $SiH_3$, $^1J_{Si-H}$ = 191.5-192.3 Hz) and $RR'_2Si$ group at δ 6.40 to -6.92. $^1H$ and $^{13}C\{^1H\}$ NMR spectra are quite straightforward and corroborate well with the composition of these compounds.

The poly(hydrosilane)s -$[RR'_2Si(CH_2)_3SiH]_n$- **13a-15a** (scheme 4) have been synthesized by dehydrocondensation of the corresponding carbosilane monomers **13-15** using catalytic amount of $Cp_2TiCl_2$/2.2BuLi. These are obtained as pale yellow viscous gums and are soluble in common organic solvents such as dichloromethane, chloroform, hexane, toluene, THF etc. GPC data reveals a monomodal molecular weight distribution in each case with Mw = 2168-2309 and PDI = 1.16-1.28.




**(13a-15a)**

R = R' = Et (**13a**); R = Ph, R' = Me (**14a**); R = Me, R' = Ph (**15a**)

**Scheme 4**

These polysilanes have been characterized by IR, multinuclear ($^1H$, $^{13}C$, $^{29}Si$) NMR as well as UV spectral studies. The Si-H groups in these polymers are identified by a characteristic IR absorption at 2095-2105 $cm^{-1}$. $^1H$, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$ NMR spectra are consistent with the composition of each polymer. In particular, DEPT-135 $^{13}C\{^1H\}$ and HSQC ($^1H$-$^{13}C$) NMR spectra are quite informative in assigning the various overlapping resonances. For example, HSQC ($^1H$-$^{13}C$) NMR spectrum (figure 8) of -$[Et_3Si(CH_2)_3SiH]_n$- (**13a**) reveals cross peaks at δ 23.26-22.38/1.38 (β-$CH_2$), 15.96-15.52/0.64 (γ-$CH_2$) and δ 7.48 ($CH_3$-Et), 14.62-13.15 (α-$CH_2$)/0.85. $^{29}Si\{^1H\}$ NMR

spectra invariably show a singlet at δ 6.96 to -7.02 and a broad complex pattern of signals at δ -57.30 to -65.70 which are attributed to the carbosilyl side groups and silicon backbone respectively. Contrary to the UV spectra of polysilanes -[MeSiR]$_n$- (R = carbosilyl; chapter 4), these polysilanes invariably show a shoulder like absorption without any peak at 250-260 nm. The 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.

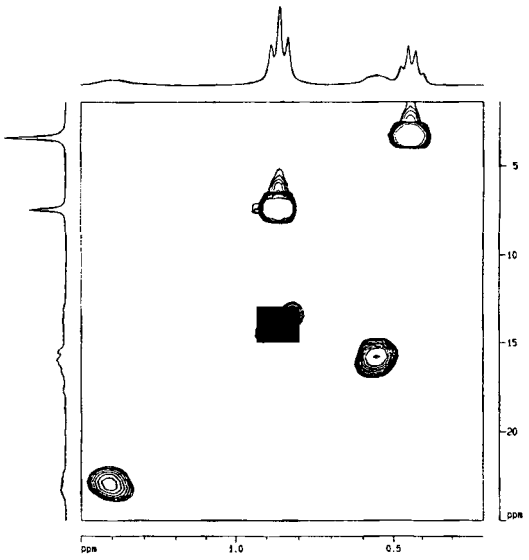
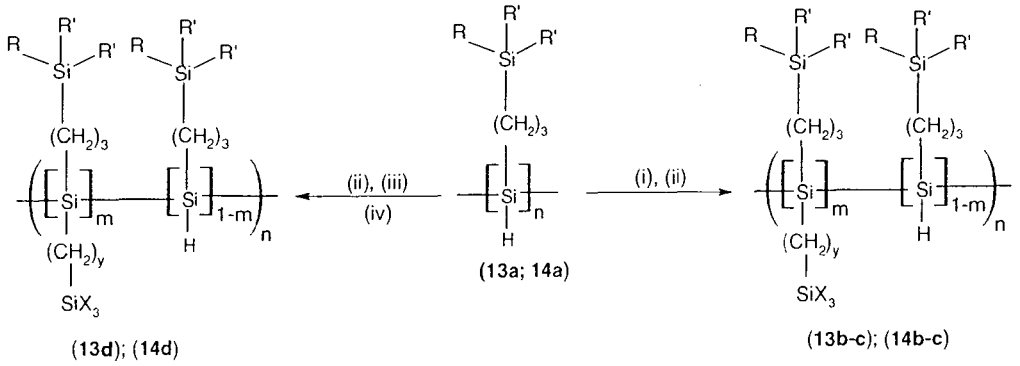



**Figure 8: ($^1$H-$^{13}$C) HSQC NMR spectrum of -[$Et_3Si(CH_2)_3SiH]_n$- (13a)**

The Si-H groups in polysilanes, -[$RR'_2Si(CH_2)_3SiH]_n$- ( R = R′ = Et (**13a**) and R = Ph, R′ = Me (**14a**)) have been subjected to chemical modification via free radical hydrosilylation reaction with allyltrimethyl/triethoxyvinyl/trichlorovinylsilane in presence of AIBN as the catalyst. This results in the isolation of new polysilanes **13b-d** and **14b-d** bearing asymmetrically substituted carbosilyl side chains (scheme 5). These polysilanes are pale yellow viscous gums and are soluble in common organic solvents such as $CH_2Cl_2$, $CHCl_3$, toluene, THF etc.




Reagents: (i)$CH_2$=$CHCH_2SiMe_3$/$CH_2$=$CHSi(OEt)_3$ (ii) AIBN (iii)$CH_2$=$CHSiCl_3$ (iv) $LiAlH_4$

| R, R' | Polysilane | X(y) | Polysilane |
|---|---|---|---|
| Et | **13a** | Me (3); OEt (2); H (2) | **13b-d** |
| Ph, Me | **14a** | Me (3); OEt (2); H (2) | **14b-d** |

**Scheme 5**

GPC analysis reveals a monomodal molecular weight distribution in each case with Mw = 2289-4780 and PDI = 1.25-1.78. An analysis of GPC data suggests that free radical hydrosilylation of the parent polymer occurs without the scission of polymer backbone. These results coupled with $^1$H NMR spectra reveal >90% inclusion of the carbosilyl moieties in the polymers. The inclusion of carbosilyl groups, such as $R_3Si(CH_2)_x$ (R = H, OEt, Me; x = 2 or 3) has been confirmed by $^1$H and $^{13}C\{^1H\}$ NMR as well as HSQC ($^1$H-$^{13}C\{^1H\}$) NMR spectra. The HSQC ($^1$H-$^{13}C\{^1H\}$) NMR spectrum (figure 9) of the polymer **13b** shows cross peaks at δ 21.88, 17.64/1.44 (β-/β′-$CH_2$), 16.61, 22.47/0.62 (γ-/γ′-$CH_2$), 20.15, 17.64, 7.54/0.94 (α-/α′-$CH_2$, $CH_3$-Et), -1.52/0.00 (Si$Me_3$), 3.46/0.51 ($CH_2$-Et) and confirms the spectral assignments based on 1D spectra. In the $^{29}Si\{^1H\}$ NMR spectra, a broad resonance due to silicon backbone appears at δ -27.23 to -30.78 in addition to characteristic signals due to the appended carbosilyl moieties. For **13d** and

**14d,** the presence of appended $SiH_3$ group is confirmed by a distinct quartet centered at δ -52.79 to -53.63 (q, $^1J_{Si-H}$ = 192.5-193.1 Hz).

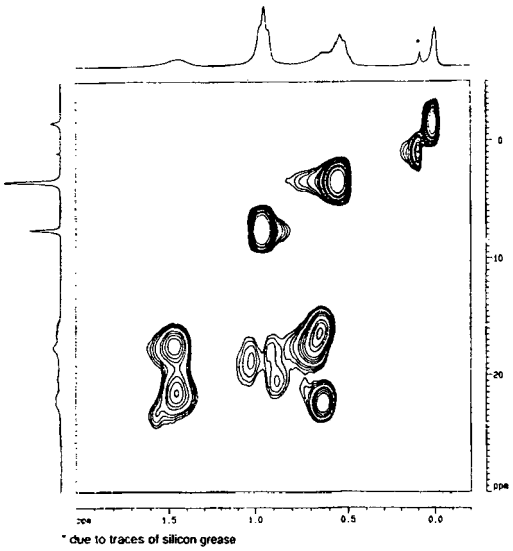



**Figure 9: ($^1$H-$^{13}$C) HSQC NMR spectrum of -[$Et_3Si(CH_2)_3Si(CH_2)_3SiMe_3]_n$- (13b)**

UV spectra of the polysilanes -[$Et_3Si(CH_2)_3SiR]_n$- [R = $(CH_2)_3SiMe_3$ (**13b**); $(CH_2)_2Si(OEt)_3$ (**13c**); $(CH_2)_2SiH_3$ (**13d**)] along with the parent poly(hydrosilane) are shown in figure 10. These modified polymers exhibit a broad and distinct absorption at $\lambda_{max}$ 274-299 nm and undergoes a bathochromic shift of the order of ~25-40 nm with respect to the parent poly(hydrosilane). This behavior may be attributed to chain stiffening of the silicon backbone due to steric effect of long carbosilyl chains which impart more extended trans conformation to the silicon backbone. The variation in the $\lambda_{max}$ values in these polysilanes may be explained by considering the steric effect of the $R_3Si$ substituents associated with the pendant carbosilyl groups. The increasing order of bathochromic shift follows the sequence $SiH_3$<$SiMe_3$~$Si(OEt)_3$.

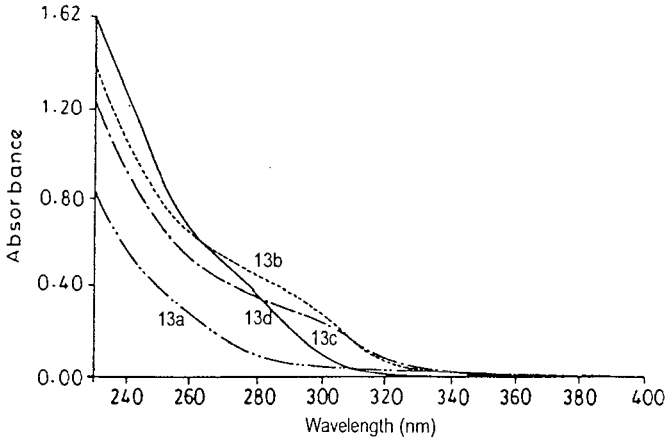
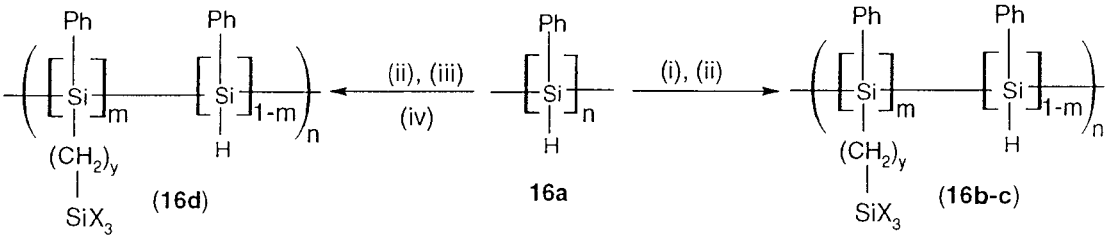



**Figure 10: UV spectra (cyclohexane, RT) of polysilanes (13a-d)**

The chemical modification approach has also been extended to poly(phenylsilane) and the resulting polymers are shown in scheme 6. GPC data shows a monomodal molecular weight distribution with Mw = 2348-7122 and PDI =1.33-2.05. The IR and multinuclear ($^1H$, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$) NMR spectral data correlates well with the composition and suggest the inclusion of 75-85 % carbosilyl moiety as the pendant groups.




Reagents: (i) $CH_2=CHCH_2SiMe_3/CH_2=CHSi(OEt)_3$/(ii) AIBN (iii) $CH_2=CHSiCl_3$ (iv) $LiAlH_4$

X = Me, y = 3 (**16b**); X = OEt, y = 2 (**16c**); X = H, y = 2 (**16d**)

**Scheme 6**

UV spectra of the chemically modified polymers (**16b-d**) reveal absorption at 314-328 nm with ε = 1500-2700 (Si repeat unit)$^{-1}dm^3cm^{-1}$ (figure 11). Interestingly, the relative

magnitude of the observed bathochromic shift in these polysilanes follows the order: **16d** (314)(**16b**(328)~**16c**(323) and correlates well with those of related polysilanes **13b-d**.

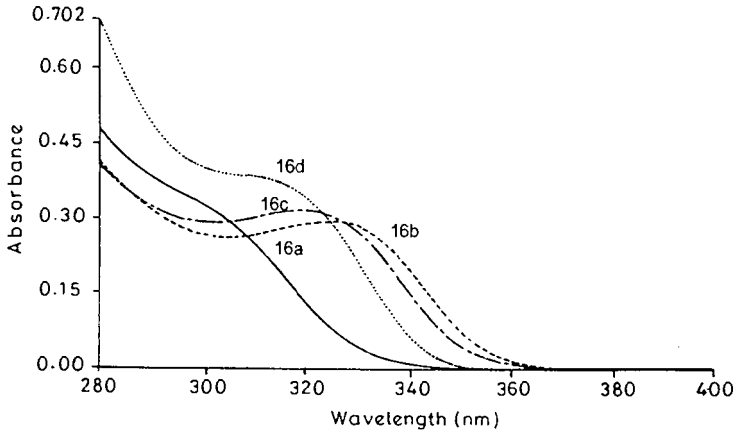



**Figure 11: UV spectra (THF, RT) of polysilanes (16a-d)**

**Glossary of Symbols and Abbreviations**

| | |
|---|---|
| Å | Angstrom |
| AIBN | 2, 2'-azobis(isobutyronitrile) |
| $\lambda_{max}$ | absorption maxima |
| b.p. | boiling point |
| br | broad signal |
| Bu | butyl |
| n-BuLi | n-butyl lithium |
| $\delta$ | chemical shift |
| J | coupling constant |
| Cat. | catalytic |
| °C | degree centigrade |
| Cp | cyclopentadienyl |
| d | doublet |
| $CH_2Cl_2$ | dichloromethane |
| DEPT | Distortionless enhancement by polarization transfer |
| EI | Electron impact |
| $\nu$ | frequency |
| FT | Fourier transform |
| fwhm | full width at half maximum |
| e.g | for example |
| Et | ethyl |
| g | gram |
| GPC | gel permeation chromatography |
| h | hour |
| Hz | Hertz |
| HSQC | heteronuclear spin quantum correlation |
| Hex | hexyl |
| IR | Infrared |
| $\varepsilon$ | molar absorptivity |
| m/z | mass/charge |

| | |
|---|---|
| m.p. | melting point |
| m | multiplet |
| *m*- | meta |
| Me | methyl |
| Mes | mesityl |
| mL | milliliter |
| mmol | milli mole |
| mol | mole |
| % | percent |
| *p*- | para |
| Mw | weight average molecular weight |
| Mn | number average molecular weight |
| nm | nano meter |
| NMR | Nuclear Magnetic Resonance |
| ORTEP | Oak Ridge Thermal Ellipsoid Plot |
| Oct | octyl |
| PDI | polydispersity |
| PL | photoluminescence |
| Ph | phenyl |
| Pr | propyl |
| q | quartet |
| RT | room temperature |
| s | singlet |
| t | triplet |
| TOCSY | Total correlation spectroscopy |
| THF | tetrahydrofuran |
| TGA | Thermogravimetric analysis |
| TMS | tetramethylsilane |
| UV | Ultraviolet |
| UPL | Ultraviolet photoluminescence |
| VPL | visible photoluminescence |

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