SYNTHETIC ASPECTS OF POLYSILANES BEARING THIENYL/FURYL-SUBSTITUTED CARBOSILYL SIDE CHAINS AND THEIR REDUCING BEHAVIOR TOWARDS Ag(I) AND Pd(II) IONS

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CERTIFICATE

This is to certify that the thesis entitled "***Synthetic aspects of polysilanes bearing thienyl/furyl-substituted carbosilyl side chains and their reducing behavior towards Ag(I) and Pd(II) ions***" being submitted by **Ms. Vandana Shahi** to the Department of Chemistry, Indian Institute of Technology, Delhi, for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by her.

Vandana Shahi has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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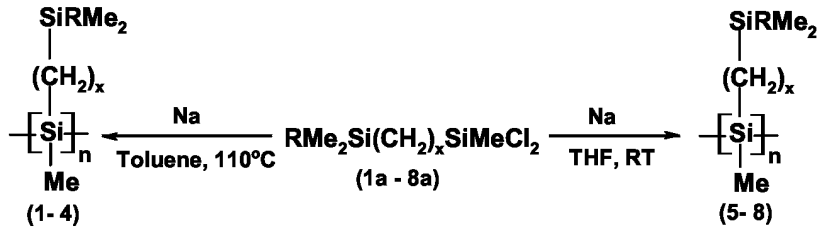
Abstract

The work embodied in the present thesis deals with a systematic study on the synthesis and characterization of new polysilanes of the general formula $[RMe_2Si(CH_2)_xSiR']_n$ (x = 2, 3; R = 2-Fu, 5-Me-2-Fu, 2-Th, 4-Me-2-Th; R' = H, Me, *n*-Hex or Ph) bearing thienyl(Th)/furyl(Fu)-substituted sila-alkyl side chains. Our interest in this class of polymers stems from the following reasons. The structural characteristics of sila-alkanes are known to differ from the corresponding *n*-alkanes and it would be of interest to comprehend the role of appended sila-alkyl groups on the electronic property associated with σ-σ* transition. The presence of sila-alkyl groups also offers the possibility to expand the scope of substitution chemistry for chemical modification of the side chain groups. While the reducing behavior of poly(diorganosilane)s towards noble metal ions such as Ag(I), Pd(II) and Au(III) has been recently reported, the need to anchor thienyl/furyl groups on the side chains has been felt in order to impart stability to the *in situ* generated metal nanoparticles in the polymer matrix. A detailed account of the results obtained during the course of the work is presented in chapters III-VI.

Chapter III - Synthesis and characterization of polysilanes $[RMe_2Si(CH_2)_xSiMe]_n$ (x = 2, 3; R = 2-Fu, 5-Me-2-Fu, 2-Th, 4-Me-2-Th) and their application in the generation of stable palladium nanoparticles

A major emphasis in this chapter is devoted to understand the scope of Wurtz coupling approach for the synthesis of functional polysilanes bearing thienyl/furyl-substituted carbosilyl side chains. As shown in scheme 1, the carbosilane monomers of general formula $RMe_2Si(CH_2)_xSiMeCl_2$, (x = 2, 3; R = 2-Fu, 5-Me-2-Fu) **1a-4a** have been synthesized and subjected to dehalocondensation with sodium dispersion in refluxing

toluene. The reaction proceeds smoothly in each case to afford high molecular weight polysilanes **1-4** in 9-15 % yield. On the other hand, analogous carbosilane monomers **5a-8a** bearing thienyl/substituted-thienyl groups are intolerant to the harsh reaction conditions and attempts to polymerize these monomers only gave an intractable solid in each case which could not be characterized. However, simple alteration of the reaction conditions (Na, THF, RT), as reported by Jones and Holder has been successful in the isolation of the desired polysilanes **5-8.** The method is also found to be advantageous in providing nearly two-fold increase in the isolable yields (20-25 %) of high molecular weight fraction.



R	x	polysilane
	2 / 3	1 /2
	2 / 3	3 / 4

R	x	polysilane
	2 / 3	5 / 6
	2 / 3	7 / 8

Scheme 1

The polysilanes **1-8** are found to be soluble in common organic solvents such as THF, toluene, dichloromethane, chloroform etc. Thermogravimetric analysis (TGA) reveals that these are stable upto 300-350 °C. However, continuous weight loss is observed till 500 °C leaving a residual yield of 12-18 %. GPC analysis reveals a monomodal molecular weight distribution in each case with M_w/PDI = 3.3-5.4 x 10^4/1.22-1.47 (for **1-4**) and 9.1-14.4 x 10^4/1.45-1.61 (for **5-8**). The $^{29}Si\{^1H\}$ NMR spectra invariably show a sharp resonance at δ -9.48 to -10.74 (for **1-4**) and -5.16 to -6.63 (for **5-8**) due to the

appended silicon atom associated with the side chain. In addition, a broad featureless signal in the region δ -27.97 to -33.56 is attributed to the skeletal silicon backbone. The electronic spectra (figure 1) associated with the σ-σ^* transition exhibit strong absorption at λ_{max} = 300-313 nm with molar extinction coefficient ε = 1495-5375 (Si repeat unit)$^{-1}$ dm^3 cm^{-1}. A comparison of these spectral features reveals a discernible red shift in the λ_{max} values of the polysilanes **2**, **4**, **6**, **8** bearing longer carbosilyl side chains, thus suggesting a more extended trans conformation of the silicon backbone in solution. The PL spectral profiles of all the polysilanes reveal Stokes shift of the order of 32-37 nm with full width at half-maximum corresponding to 20-28 nm. The observed emission profiles are not mirror images of the corresponding UV absorption spectra, suggesting a random coil conformation of the silicon backbone in solution.

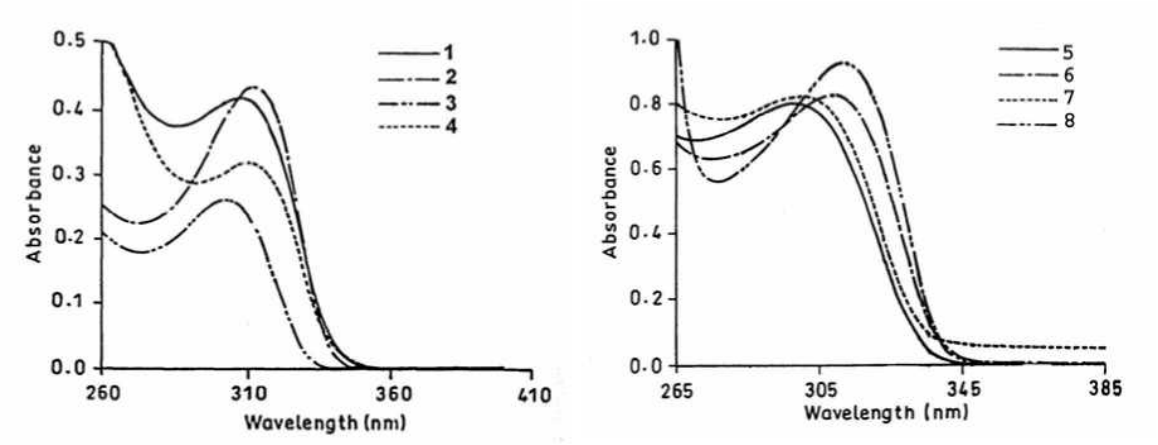


Figure 1: UV spectra (THF, RT) of polysilanes 1-8

One of the goals for the synthesis of furyl/thienyl-substituted polysilanes is to address their application in the generation and stabilization of noble metal nanoparticles. In a case study, a solution of palladium acetate in toluene upon treatment with ten monomer equivalents of the polysilane $[(2\text{-Fu})Me_2Si(CH_2)_3SiMe]_n$ **2** reveals a gradual color change from yellow to golden brown. UV-Vis spectra of the resultant solution at different time

intervals show a gradual disappearance of the band at ~400 nm due to palladium acetate. This is replaced by a monotonically broad spectrum typical of palladium nanoparticles after 24 h, suggesting the complete reduction of Pd(II) ions. Transmission electron microscopy (TEM) and dynamic light scattering (DLS) studies reveal the formation of monodispersed spherical palladium nanoparticles with an average size of 8.2 ± 0.6 nm. The polymer-Pd nanocomposite thus obtained remains stable in solution for several weeks without any precipitation of the nanoparticles. The role of the furyl group in the stabilization of Pd nanoparticles has been substantiated by studying the reaction of palladium acetate with the polysilane $[PhMe_2Si(CH_2)_3SiMe]_n$ (M_w = 6.7 x 10^4, PDI = 1.42), which is devoid of a donor substituent on the side chain. Although the polymer brings about reduction of Pd(II) ions, the *in situ* generated palladium particles undergo fast agglomeration and precipitation starts within a few hours. It has been suggested that the stability of the metal nanoparticles in the matrix derived from polysilane **2** is imparted by the donor-acceptor interactions between the furyl groups and the metal nanocluster surface.

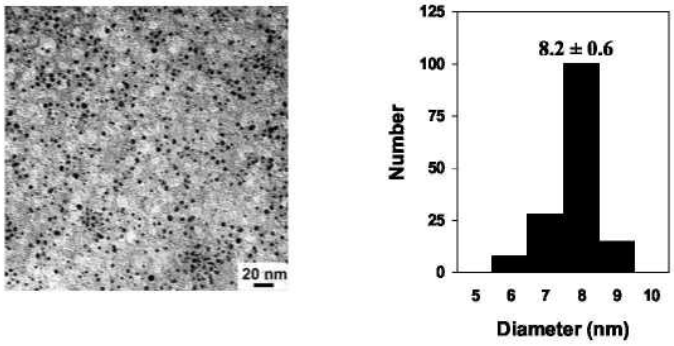
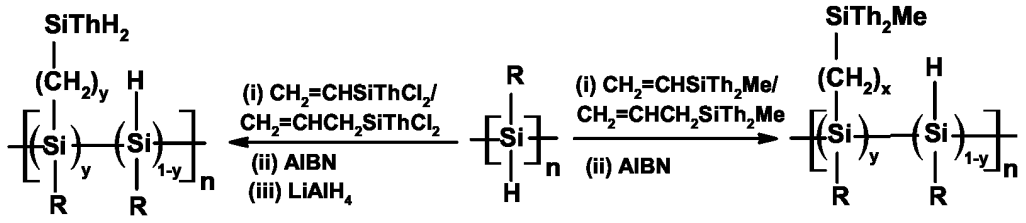


Figure 2: TEM image and particle size distribution of palladium nanoparticles in polysilane 2 matrix

Chapter IV - Synthesis and characterization of polysilanes $[(RR'_2Si(CH_2)_xSiR^1)_y(R^1SiH)_{1-y}]_n$ (x = 2, 3; R, R' = 2-Th, Me, H; R^1 = *n*-Hex, Ph) and their application in the generation of stable silver nanoparticles

Synthesis of short chain oligosilanes, bearing appended thienyl (Th) groups on the carbosilyl side chains has been achieved by chemical modification of the Si-H groups in preformed poly(*n*-hexylsilane)/poly(phenylsilane) via hydrosilylation with (2-thienyl)dichlorovinylsilane/ (2-thienyl)allyldichlorosilane/ bis(2-thienyl)methylvinylsilane/ bis(2-thienyl)allylmethylsilane using AIBN as the free radical catalyst (scheme 2). These polysilanes are important new additions amongst the family of functional polysilanes which have been synthesized via this synthetic protocol.



R	x	polysilane
n-Hex	2 / 3	9 / 10
Ph	2 / 3	13 / 14

R	x	polysilane
n-Hex	2 / 3	11 / 12
Ph	2 / 3	15 / 16

Scheme 2

The polysilanes obtained above are either pale yellow viscous gums (**9-12**) or solids (**13-16**) and are soluble in common organic solvents like dichloromethane, chloroform, toluene, THF etc. The GPC data (M_w/PDI = 2492-3080/1.18-1.44 for **9-12** and 2861-5243/1.26-1.79 for **13-16**) of all these polysilanes and the precursor polymers suggest that hydrosilylation reaction proceeds without any cleavage of the silicon backbone. It is however important to mention that quantitative conversion of the Si-H to Si-C bonds is not observed and residual Si-H groups are detected in the IR (2090-2105 cm^{-1}) and ^1H

NMR (δ 3.48-3.54) spectra. The assignment of various overlapping ^{1}H and $^{13}C\{^{1}H\}$ resonances in the alkyl region has been made by studying the (^{1}H-^{13}C) HSQC NMR spectra. The $^{29}Si\{^{1}H\}$ NMR spectral data [δ -23.80 to -33.64 (*Si*C_2 backbone), -50.07 to -54.21 (H*Si*C backbone), -35.88 to -37.00 (*Si*ThH_2)/-13.69 to -15.50 (*Si*$MeTh_2$)] are consistent with the composition of each polymer.

A qualitative estimate of the role of appended carbosilyl groups on the optical properties of the polysilanes has been made by studying the σ-σ* electronic transitions in the UV spectra. As shown in figure 3, these polysilanes reveal a discernible red shift of the absorption maxima [λ_{max} (nm)/ ε (Si repeat unit)$^{-1}$ dm^3 cm^{-1}: 284-294/789-944 (**9-12**), 315-325/1530-2830 (**13-16**)] in comparison to those observed for the parent polymers. These results are suggestive of a more extended trans conformation of the silicon backbone in the modified polysilanes.

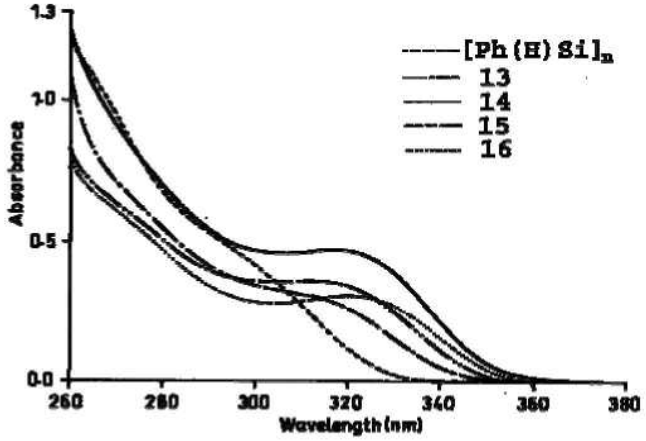
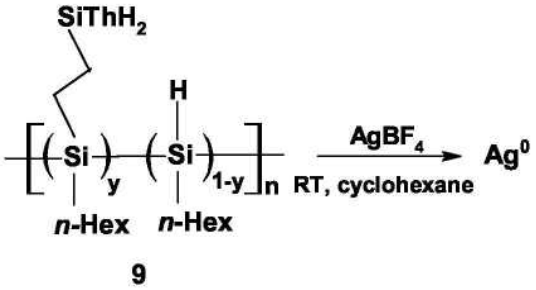


Figure 3: UV spectra (THF, RT) of polysilanes 13-16

The synthesis of silver nanoparticles involves the reaction of a suspension of silver tetrafluoroborate in cyclohexane with two monomer equivalents of polysilane [{(2-Th)H_2Si$(CH_2)_2$Si(*n*-Hex)}$_y${HSi(*n*-hex)}$_{1-y}$]$_n$ **9** (scheme 3). Gradual appearance of yellow color in the solution along with observed plasmon resonance band at ~420 nm confirms

the formation of silver nanoparticles. Time dependent UV-Vis spectral study of the polymer-Ag nanocomposite is shown in figure 4.



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Scheme 3

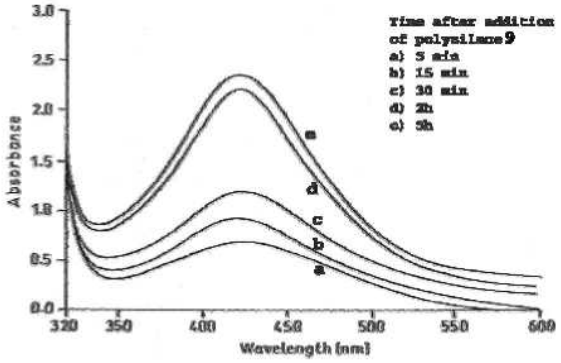


Figure 4: Monitoring of plasmon resonance band of silver nanoparticles in polysilane 9 matrix (in cyclohexane)

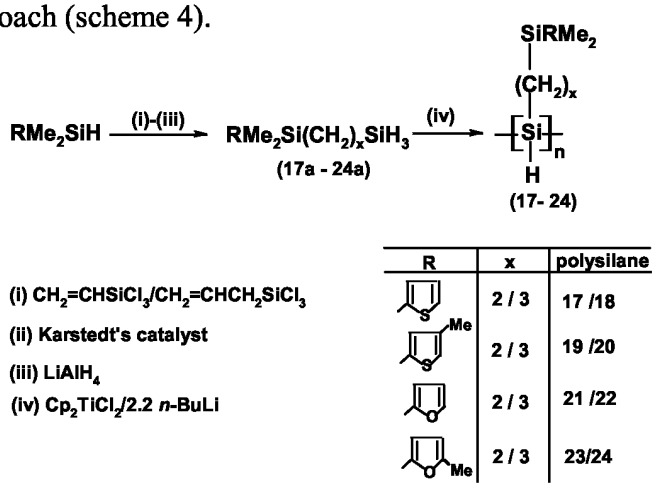
Transmission electron microscopy (TEM) and dynamic light scattering (DLS) studies show the formation of spherical silver nanoparticles with an average particle size of 8.4 ± 0.7 nm. The silver nanoparticles remain stable in solution and exhibit no sign of agglomeration even after three months. The role of the side chains bearing thienyl substituents in the polymer is found to be crucial in the stabilization of silver nanoparticles. Further validation of this behavior comes from the reaction of silver tetrafluoroborate with analogous polysilane $[\{MeH_2Si(CH_2)_2Si(n\text{-Hex})\}_{0.6}\{HSi(n\text{-hex})\}_{0.4}]_n$, which is devoid of any donor functionality. The silver nanoparticles formed in this case are much larger in size (75.5 ± 4.9 nm) even in the fresh samples and undergo precipitation within 5-7 days.

Since the reduction of Ag(I) ions involves σ-electrons of the catenated silicon backbone, the process must be accompanied by oxidation of the parent polysilane. Studies based on IR and UV spectra as well as GPC of the polymer residue obtained after precipitation of the silver nanoparticles from THF solution reveal the following features: (a) A marked

decrease in the molecular weight (M_w/PDI=1864/1.64) in comparison to that of the parent polysilane (M_w/PDI= 2500/1.32) is observed, suggesting that the reduction process is accompanied by some degree of chain scission of the silicon backbone. (b) The presence of short chain oligosilanes in the polymer-metal nanocomposite is evident from the observed UV absorption (λ_{max} = 284 nm) associated with σ-σ* transition of the catenated silicon backbone. (c) The detection of siloxane group (νSi-O-Si ~ 1080 cm^{-1}) in the IR spectrum is obscured by the presence of other absorptions due to alkyl and Si-Th groups.

Chapter V - Synthesis and characterization of poly(hydrosilane)s $[RMe_2Si(CH_2)_xSiH]_n$ (x = 2, 3; R = 2-Th, 4-Me-2-Th, 2-Fu, 5-Me-2-Fu)

In order to examine the scope of catalytic dehydrocoupling as an alternate synthetic route to polysilanes bearing appended thienyl/furyl groups on the carbosilyl side chains, the carbosilane precursors **17a-24a** with terminal SiH_3 group are obtained by using hydrosilylation approach (scheme 4).



Scheme 4

All the carbosilanes obtained above are colorless, distillable liquids and their identity has been unequivocally established from the observed molecular ion (M^+) peak in the ES (product ion) mass spectra. The ^1H and $^{13}C\{^1H\}$ NMR spectra are quite straight forward

and corroborate well with the suggested composition. For **19a** and **20a**, two distinct signals are observed due to *Me*-Th group at δ 2.30-2.37 and 15.04-16.58 in the ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra respectively, suggesting the presence of two isomers $RMe_2Si(CH_2)_xSiH_3$, [R = 4-Me-2-Th (85%), 3-Me-2-Th (15%)]. The ^{29}Si NMR spectrum of each carbosilane exhibits a distinct resonance at δ -5.56 to -6.42 (*Si*Th)/ -8.52 to -10.92 (*Si*Fu) due to SiC_4 moiety while the SiH_3 groups are discernable at δ -56.96 to -60.18.

These carbosilanes have been subjected to dehydrocoupling in presence of catalytic amount of Cp_2TiCl_2/ *n*-BuLi (40:1:2.2) under mild conditions (50 °C, 48 h). In all cases, the reaction was found to proceed smoothly and the corresponding poly(hydrosilane)s **17-24** have been isolated as orange-yellow viscous oils in 47-62% yield (scheme 4).

The polysilanes obtained above are soluble in common organic solvents such as dichloromethane, chloroform, THF, toluene, hexane etc. The GPC analysis reveals a monomodal molecular weight distribution in each case with M_w = 1625-2461 and PDI = 1.19-1.53. The SiH groups in these polymers are identified by characteristic IR absorptions at 2090-2105 (νSiH) and 910-915 (δSiH_2) cm^{-1}. ^{1}H, $^{13}C\{^{1}H\}$ and $^{29}Si\{^{1}H\}$ NMR spectra are consistent with the composition of each polymer.

The UV spectra of poly(hydrosilane)s **17-24** exhibit a weak, shoulder like absorption at 250-270 nm which is a characteristic feature of previously reported poly(hydrosilane)s with predominantly gauche conformation of the silicon backbone. Photoluminescence spectra of these poly(hydrosilane)s (cyclohexane, RT) reveal weak, broad (fwhm ~ 85-95 nm) and highly Stokes shifted (140-150 nm) emission profiles. The results parallel with that of permethyloligosilanes reported by Michl et al. By analogy, the PL behavior of

these poly(hydrosilane)s have been attributed to a non-vertically excited σ-σ* state of a lower energy arising due to a stretched Si-Si bond ("self trapped exciton")

The choice of carbosilane monomers in the present study is of significance to achieve the desired polysilanes via dehydrocoupling approach. To better understand the role of monomers, an analogous reaction of 2-thienylsilane with the Ti-catalyst has been studied. It has been observed that the reaction fails to yield the desired polysilane even after prolonged reaction conditions. A plausible explanation for this passive behavior has been sought by considering the well known mechanism for dehydrocoupling of primary silanes as proposed by Tilley et al. which takes into account the σ-bond metathesis pathway. It is proposed that intramolecular coordination of the sulfur atom of the 2-thienyl moiety to the Ti- center of the intermediate metal-silyl complex (chart 1a) impedes the step growth polymerization of 2-thienylsilane. In the case of dehydrocoupling of the carbosilanes, the metal-silyl complex remains unaffected since such a coordination is prevented due to the separation of the thienyl group from the active silicon center by $Si(CH_2)_x$ spacers.

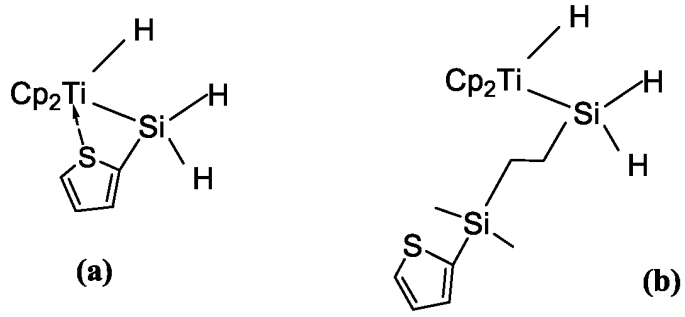
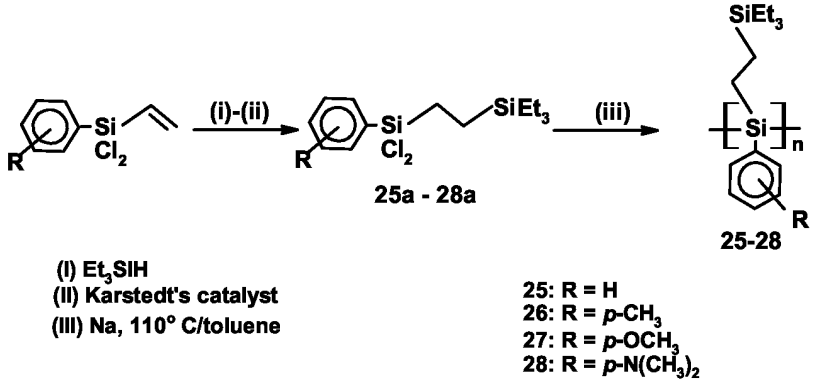


Chart 1: Proposed intermediates in the catalytic dehydrocoupling of (a) 2-thienylsilane and (b) carbosilane.

Chapter VI – Synthesis and characterization of polysilanes $[Et_3Si(CH_2)_2Si(C_6H_4R)]_n$ (R = H, *p*-Me, *p*-OMe, *p*-NMe_2) and their application in size-controlled synthesis of Ag and Pd nanoparticles

An interesting aspect of poly(dialkyl/alkylarylsilane)s relates to their HOMO-LUMO band gap energies associated with σ-delocalized silicon backbone. It has been reported earlier that a subtle change in the electronic attributes of aryl side chain substituents in poly(arylmethylsilane)s gives rise to large variations in the oxidation potential which lie between 0.23-0.81 V vs SCE. Our attempts have been focused to utilize this property of polysilanes in the generation of metal nanoparticles with special emphasis to understand if there exists a correlation between the band gap energies of polysilanes and their reducing behavior towards redox active metal ions.

A schematic presentation for the synthesis of new polysilanes, $[Et_3Si(CH_2)_2Si(C_6H_4R)]_n$ [R = H (**25**), *p*-Me (**26**), *p*-OMe (**27**), *p*-NMe_2 (**28**)] is shown in scheme 5. As evident from the GPC data, the molecular weight distribution is largely monomodal with M_w and PDI values ranging between 2.9-4.6 x 10^3 and 1.41-1.57 respectively.



Scheme 5

The chemical composition of each polymer has been elucidated by IR and multinuclear (^1H, $^{13}C\{^1H\}$ and $^{29}Si\{^1H\}$) NMR spectroscopy. A detailed analysis of the electronic

absorptions associated with the σ-σ* transition [λ_{max} (nm)/ε ((Si repeat unit)$^{-1}$dm^{3}cm^{-1}) = 320-342/ 2100-3106] (figure 5) reveals a distinct correlation between the λ_{max}/ ε values and the nature of substituents on the aryl rings. The absorption maxima undergo a progressive bathochromic shift with increasing electron-donating strength of the aryl substituent and follow the order **25** ≈ **26** < **27** < **28** (table 1). By analogy with literature precedence, these results provide a fairly good evidence of variable HOMO-LUMO band gap energies and a measure of the relative oxidation potentials of these polysilanes which are expected to follow the order, **28** < **27** < **26** ≈ **25**.

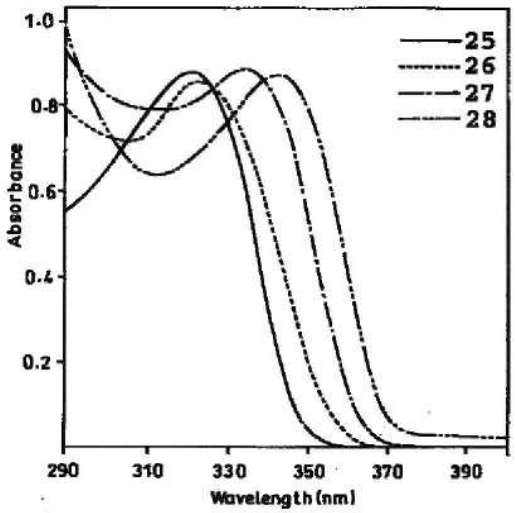


Figure 5: UV spectra (THF, RT) of polysilanes 25-28

This intrinsic property has been found to influence the particle size domains of the *in situ* generated Ag and Pd nanoparticles obtained from the reactions of $AgBF_4$ or $Pd(OAc)_2$ with different polysilanes under ambient conditions (RT, cyclohexane or toluene). The results obtained from TEM and DLS studies are shown in figure 6 and the relevant data is summarized in table 1. The results reveal that size domain of both Ag (7.4-22.7 nm) and Pd (27.8-41.0 nm) nanoparticles progressively gets larger as the reducing strength of the polysilane decreases. Although a similar correlation between the oxidation potential and

size domains has been reported earlier using the family of reducing agents derived from carboxylates and polyoxometalates, the use of polysilanes for size-controlled synthesis of metal nanoparticles is being observed for the first time. These results are in accord with the general concept that stronger reducing agents result in faster rate of nucleation in comparison to particle growth and consequently afford the formation of smaller nanoparticles.

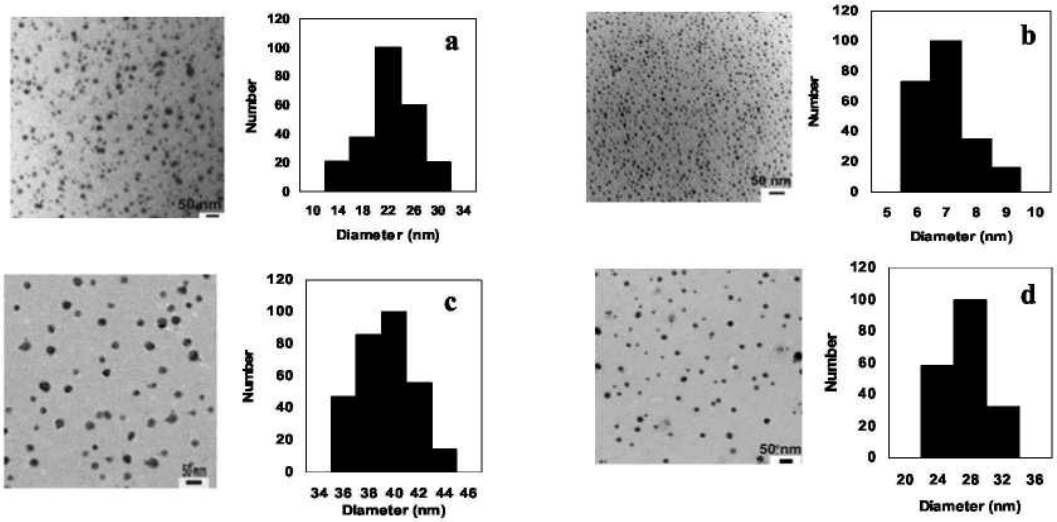


Figure 6: TEM images and particle size distribution of silver nanoparticles in (a) polysilane 26 matrix (b) polysilane 28 matrix and palladium nanoparticles in (c) polysilane 26 matrix (d) polysilane 28 matrix

Table 1: GPC and UV characteristics of polysilanes 25-28, particle size of *in situ* generated Ag and Pd nanoparticles

Polysilane $[Et_3Si(CH_2)_2Si(C_6H_4R)]_n$		UV[a] $\lambda_{max}/\varepsilon$	Particle size[b] (nm)	
			Ag	Pd
R = H	**25**	320 / 2100	22.7 (2.4)	41.0 (3.0)
R = *p*-Me	**26**	323 / 2330	22.3 (4.2)	39.5 (2.8)
R = *p*-OMe	**27**	332 / 2986	11.4 (2.1)	32.6 (2.0)
R = *p*-NMe_2	**28**	342 / 3106	7.4 (0.9)	27.8 (2.8)

[a] λ_{max} units: nm; ε units: (Si repeat unit)$^{-1}$ dm^3 cm^{-1}.
[b] From DLS studies; the figures in parentheses indicate the standard deviation

The compositional aspect of the oxidized polymer matrix which hosts the metal nanoparticles in the polymer-metal nanocomposite has been studied by ^{29}Si NMR and UV-Vis spectral studies. Interestingly, the results reveal the presence of short chain silicon catenates as an integral part of the host matrix in addition to cyclic/linear siloxanes. Although, the limiting value of the chain length in these cases is not yet established, it is apparent that the oxidation of shorter length segments derived during the reduction of the metal ions is not favored. A possible explanation for the low affinity of the short chain catenates towards oxidation may be sought by considering the earlier report by Miller et al. on the electrochemical studies of poly(methylphenylsilane). It has been reported that oxidation potential of the short chain silicon catenates formed upon electro-oxidation of high molecular weight poly(methylphenylsilane) increases to 1.1 V in comparison to that of the parent polymer (0.79 V), thereby rendering the oligomers less prone to oxidation. By analogy, in the present case as well it may be concluded that the short chain oligosilanes in the oxidized matrix do not participate in the reduction of Ag(I) and Pd(II) ions and hence remain an integral part of the polymer composition.

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