

Novel electrochemical synthesis and characterisation of poly(methyl vinylsilane) and its co-polymers

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Abstract

The electrochemical synthesis and characterisation of poly(methyl vinylsilane) and a series of poly(methyl vinylsilane-co-metallocenes) network polymers are described in detail. This class of polymers are not accessible through Wurtz coupling reaction and are however prepared by electro-reduction of dichloro methyl vinylsilane in a non-aqueous system using aluminum electrodes in a single compartment cell. These polymers have been characterised using UV, FTIR, XRD, SEM and NMR spectral techniques. Cyclic voltammetric studies of the above polymers reveal their conducting behavior. These polymers show optical properties as explained from the results. Polymers of this type are proposed as potential soluble precursors for SiC and metal doped SiC materials.

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1. Introduction

Polysilanes consisting of Si–Si σ bonds synthesised using the most general method namely Wurtz coupling reaction of organodichlorosilane with alkali metals [1]. However this approach has several difficulties and disadvantages in controlling the unit-structure, molecular weight, polymerisation of monomers possessing functional groups and also to control dispersity of the polymers [2]. The yield of polymers is also usually low and alkali metal reduction does not seem to be easily industrialized in large scale because of the risk involvement of

alkali metals and high reaction temperature in the case of Na and K. To circumvent various set backs mentioned in the Wurtz type synthesis, several novel methods have opened new approaches for the synthesis of structure-ordered polysilanes, which are essential to the further development in the polysilane chemistry [3]. Recently, it has been demonstrated that compounds with Si–Si bonds are produced in good yields by the electrolytic reduction of dichlorosilanes in an undivided cell using a sacrificial metal anode such as mercury, aluminum, magnesium, silver and copper or using hydrogen electrodes [4–6]. Poly(methylsilane) and poly(cyclohexylsilane-co-methylsilane) network co-polymers were prepared by electrochemical reduction of methyltrichlorosilane, or mixture of the monomers methyltrichlorosilane and cyclohexyl trichlorosilane, utilizing copper electrodes. Poly(methylsilane) synthesised through Wurtz coupling technique is proposed as the potential soluble precursor for SiC [7]. Polygermane and

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germane–silane co-polymer have been prepared electrochemically using magnesium electrodes. These polymer materials are having promising physical properties such as semiconductivity, photoconductivity, photoluminescence and third-order non-linear effects [8].

There has been a great deal of interest in the synthesis and application of various luminescent compounds of silicon, particularly polysilanes because of their unique aspects regarding spatial confinement and dimensionality [9–14]. Yamabe et al. [15] have investigated theoretically the relationship between the structure of organosilicon polymers and the band gap energy. They predicted that a hypothetical polymer consisting of Si–Si single bonds and C=C double bonds alternately would have the lowest band gap energy. Therefore, many types of organosilicon polymers comprising Si–Si bonds have been prepared, and their potential as conducting polymers was investigated [16–19]. Increasing attention has also been directed towards synthesising organosilicon compounds and their photoluminescence as well as the possibility of making efficient room-temperature light emitting devices [12]. Photoluminescence is important not only to understand the origin but also to make efficient opto-electronic devices [20].

Metal containing polymers of poly(ferrocenes), poly(ferrocenyilsilanes) and zirconocene containing polymers have been prepared and characterised. These polymers are of great importance because of their potential uses as electroactive sensors, catalysts, polymer supported electrodes, photosensitizers, synthetic precursors, etc. [21]. Edirsinghe et al., have synthesised poly(methyl vinylsilane) using alkali dechlorination of dichloro methylvinylsilane in refluxing toluene/THF with molten Na metal. The obtained poly(methyl vinylsilane) was used to develop SiC foam using polyurethane sponge in dichloromethane. This pre-foam was subsequently pyrolysed under N₂ atm. at the temperature range of 900–1300 °C [22]. Photocarrier generation at nano-interfaces in organic polysilane–titania matrix hybrid thin films was also studied recently by Satoshi Miura [23].

The electronic structure and spectral properties of polysilanes more closely resemble those of conjugated π -systems such as polyacetylenes. There have been several reports regarding charge transfer from the Si–Si σ bond to the aromatic moiety in the excited state [24]. Polysilane containing anthracene units have attracted much attention as σ – π conjugated organosilicon polymers, which have a possible application as electro luminescence materials, because of these polysilanes will be regarded as organic semiconductors with high photoluminescence quantum efficiency. Here, we report for the first time, the electrosynthesis, characterisation and photoelectronic properties of poly(methyl vinylsilane) and its co-polymers of poly(methyl vinylsilane-co-ferrocene), poly(methyl vinylsilane-co-titanocene) and poly(methyl vinylsilane-co-zirconocene).

2. Experimental

2.1. Materials

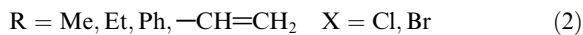
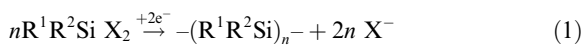
Dichloro methyl vinylsilane, dicyclo pentadienyl iron(ferrocene), dicyclo pentadienyl titanium dichloride (titanocenedichloride) and dicyclo pentadienyl zirconium dichloride (zirconocene dichloride) were used as the monomers for preparing corresponding polymers. Tetrabutylammonium tetrafluoroborate (TBATFB) was precipitated in pentane-ethyl acetate solution and dried in vacuum before using as a supporting electrolyte. 1,2-dimethoxyethane (DME) was further purified by treating with LiAlH₄ for 3 h and fractionally distilled at 70 °C immediately before making solutions. The purity of the monomer dichloro methylvinylsilane was checked with HPLC and was found to be 98% pure.

2.2. Electrochemical setup

All reactions were carried out under dry nitrogen atmosphere in a single compartment cell equipped with pure aluminum rods of area 5.9 cm² and 30 cm² as cathode and anode respectively. The supporting electrolyte was 0.4 M TBATFB in 1,2-dimethoxyethane.

2.3. Electropolymerisation and isolation

All reactions were carried out in the dark in order to avoid any photochemical reactions. Twenty five milliliter of TBATFB in DME, previously dried under vacuum for 3 h, was placed in the electrochemical cell and dried again in the cell under vacuum for 1 h. Typically 0.08 M of the dichloro methyl vinylsilane was introduced into the cell. Before adding the starting material dry nitrogen gas was purged into the cell containing the supporting electrolyte for 1 h to eliminate the dissolved oxygen, which will interfere in the reaction, and form polysiloxane as the product instead of forming polysilane [25,26]. The amount of the introduced starting compound was calculated from the weight increase of the entire cell assembly. Electrolysis was carried out at room temperature and at constant current electrolysis technique. The current density was fixed at 4.5 mA/cm² and the charge consumed during the reaction was 2 F/mol. based on Eq. (1)



After electrolysis, the solution was concentrated to half of the original volume under reduced pressure and poured into 300 ml of methanol. The polymer precipitated in methanol (TBATFB was dissolved in methanol and separated from the polymer) then the polymer was

Table 1
Molecular weight, UV absorption and bandgap datas of the metal-containing polymers

Sl. no	Polymer	Metallocene conc. (M)	Molecular weight	M_w/M_n	λ_{\max} (nm) Si-M	Bandgap (eV)
1	Poly(methyl vinylsilane)		16,850	1.0354	260 315 364	1.5
2	Poly(methyl vinylsilane-co-ferrocene)	0.005	9013	1.0566	272 320 363	2.0
		0.01	13,456	1.0375	363 325 278	1.9
		0.02	20,280	1.0432	275 328 431	1.75
3	Poly(methyl vinylsilane-co-titanocene)	0.005	8950	1.0365	308 362	2.9
		0.01	14,692	1.0548	312 365	2.85
		0.02	20,020	1.0588	262 315 369	2.0
4	Poly(methyl vinylsilane-co-zirconocene)	0.005	10,250	1.0453	318 362	3.3
		0.01	16,885	1.0966	308 362	3.0
		0.02	23,760	1.0754	260 279 312 365	2.4

Concentration of chloro methyl vinylsilane = 0.08 M.

collected and redissolved in 50 ml of toluene. The toluene solution was poured into 300 ml of methanol. Such a dissolution and precipitation procedure was repeated thrice. Finally, the collected polymer was dried in vacuum [24].

The reaction gives the polymer with the yield of 76%. Its molecular weight is 16,850 and its M_w/M_n is 1.0354.

Additionally, electrolysis was also carried out in the same manner to synthesis co-polymers using various metallocenes such as ferrocene, titanocene dichloride and zirconocene dichloride.

In this, electrolysis was carried out using the supporting electrolyte (0.4 M TBATFB in DME) and 0.08 M dichloro di methyl vinylsilane as the starting material. Ferrocene (0.005 M) was introduced into the cell containing the above supporting electrolyte. Electrolysis was carried out using a similar procedure and the yield

was 81%. Molecular weight of the polymer was 9013 and its M_w/M_n was found to be 1.0463.

A similar experiment was carried out using various concentrations of ferrocene such as 0.01 M, 0.02 M which gave better yields and their molecular weights were 13,456 and 20,280 respectively and M_w/M_n were 1.0395 and 1.0432 respectively. Similarly the other co-polymers were synthesised using the above technique.

2.4. Characterisation of polymer

Identification of polymers was carried out by comparing their properties with the reported values. Poly(methyl vinylsilane) and its co-polymers were identified using GPC (Shimadzu, LC-6A, Japan), UV (Hitachi V-3400, Japan), FTIR (Perkin Elmer, paragon-500, England), and ^1H NMR (BRUCKER, 350 MHz, Japan)

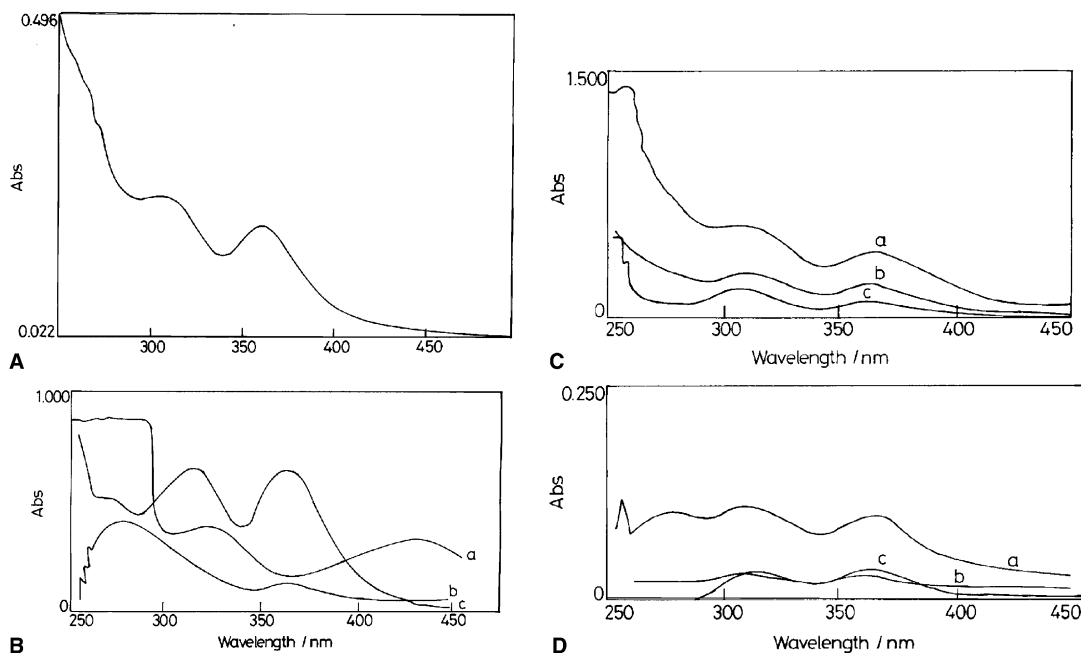


Fig. 1. UV-Vis absorption spectra of (A) poly(methyl vinylsilane); (B) poly(methyl vinylsilane) co-polymer with ferrocene (C) poly(methyl vinylsilane) co-polymer with titanocene and (D) poly(methyl vinylsilane) co-polymer with zirconocene [at different concentrations: (a) 0.02 M, (b) 0.04 M, (c) 0.08 M].

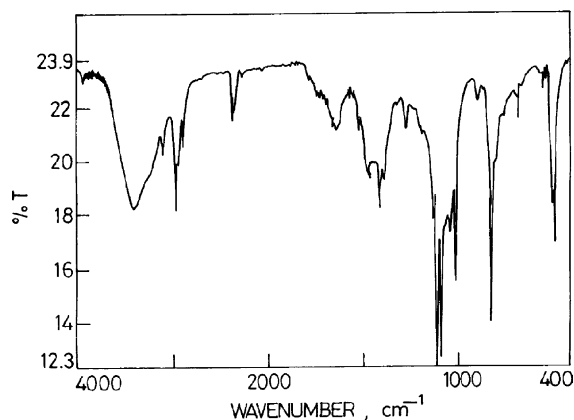


Fig. 2. FTIR spectrum of the powder samples of poly(methyl vinylsilane).

spectral techniques. UV spectra were measured in tetrahydrofuran unless otherwise stated because it dissolves variety of polysilanes. FTIR spectra were measured using KBr method. ^1H NMR spectra were measured in CDCl_3 . Molecular weights were determined by gel-permeation chromatography relative to polystyrene standards.

3. Results and discussion

3.1. Synthesis of poly(methyl vinylsilane)

Synthesis of poly(methyl vinylsilane) gave the best results i.e. relatively high yield, high molecular weights and long absorption λ_{max} as reported in Table 1. This polymer precipitated as colorless solid in methanol, and is appeared to be stable in the atmosphere [27]. The polysilanes are different from all other high polymers, in that way exhibit sigma electron delocalization. When polysilane absorb energy in the ultraviolet region, electrons are promoted from σ -valence band to the σ^* conduction band [28]. Since UV-Vis spectrum of organo polysilanes shows its absorption maxima ranging from 280 to 350 nm [23,29–32], peaks for poly(methyl vinylsilane) absorbed near 364 nm and 315 nm (Fig. 1A) can be attributed to Si-Si main chain of trans and gauche states respectively [29]. This red shift with increasing molecular weight observed in the poly(methyl vinylsilane) is due to the delocalization of σ -electrons in the Si-Si main chain of the polymer, and thus it strongly exhibit an intense σ - σ^* transition at 364 nm [4,20,30]. Co-polymers of poly(methyl vinylsilane-co-metalloenes), such as ferrocene, titanocene and zirconocene absorbs in the same region because of the presence of more trans Si-Si-Si conformation [31]. Absorption behavior and conducting properties of metal-containing polymers can change

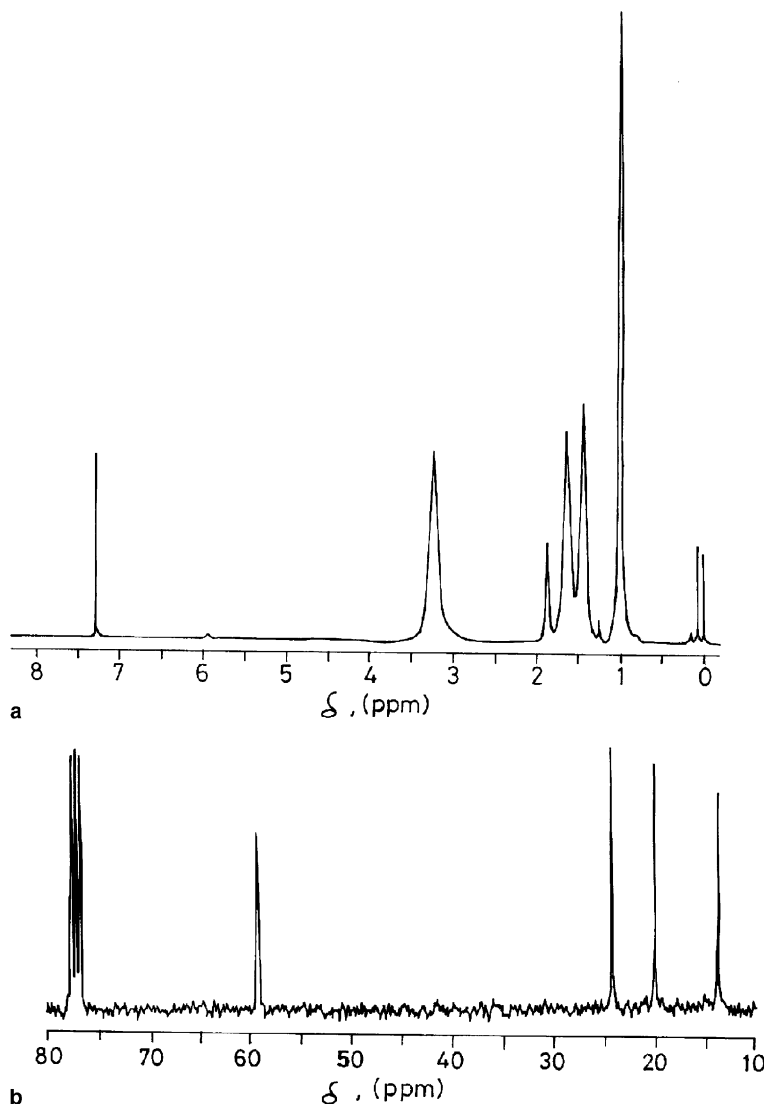


Fig. 3. NMR profiles of the powder samples of poly(methyl vinylsilane): (a) ^1H NMR data and (b) ^{13}C NMR data.

appreciably according to the Si–metal bond type in the polymer chain. Since λ_{max} values for the σ/π zirconocene containing polymers are found to be between 214 and 266 nm [32], peaks for the poly(methyl vinylsilane-co-zirconocene) observed near 315 nm (Fig. 1D) can be attributed to silane–zirconocene co-polymer formed in the procedure. And it also stated that, the longer absorption of the doped polysilane indicate that more charge transfer complex was formed on the side groups of the polysilane and hence cause an increase in the conductivity [33]. The other metal containing polymers such as σ/π ferrocene-containing polysilane and σ/π titanocene-containing polysilane show specific absorption near 318–330 nm and 310 nm respectively (Fig. 1B–C). This metal

containing polysilane shows similar absorption behavior and conducting properties, due to their σ/π conjugated nature. According to Table 1, all these polymers show high band gap energies. That means, there is little or no conjugation between monomer units [32]. As the concentration of dopant decreases, the intensity of absorption also decreases, which in turn indicates a decrease in the molecular weight of polymer (Table 1) [23,33,34].

The fourier transform infrared spectrum (Fig. 2) indicates that the poly(methylvinylsilane) has Si–CH₃ (815 and 1261 cm^{-1}), Si–CH (1105 cm^{-1}), C–H bending (2962 cm^{-1}) groups. The absorption at 3400 cm^{-1} may be due to the moisture absorption of the starting material. Here Si–Cl (662 cm^{-1}) is completely absent [35]

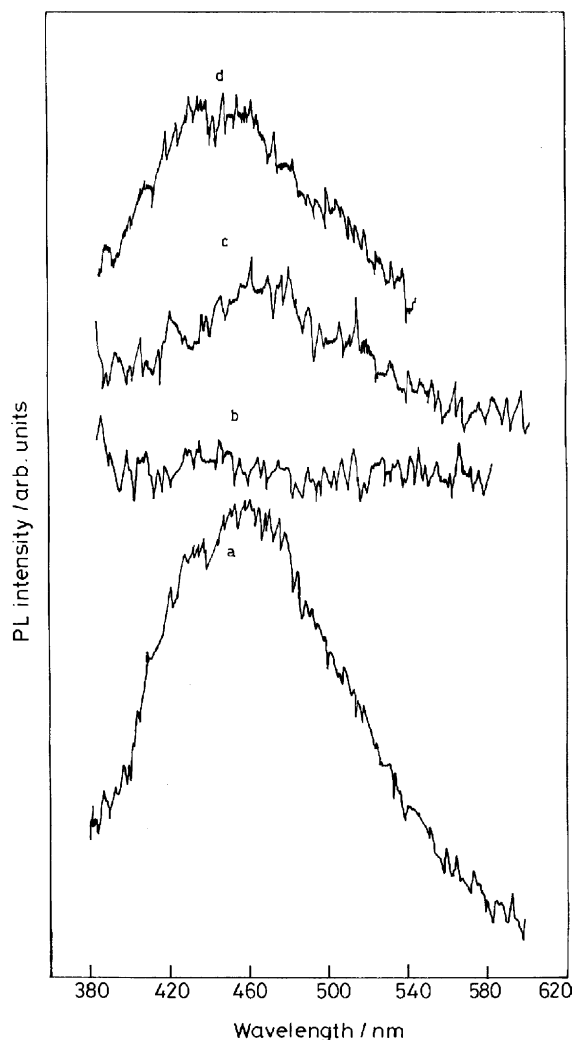


Fig. 4. Photoluminescence spectrum of (a) poly(methyl vinylsilane), (b) poly(methyl vinylsilane) doped with ferrocene, (c) poly(methyl vinylsilane) doped with dicyclo pentadienyl titanium and (d) poly(methyl vinylsilane) doped with dicyclo pentadienyl zirconium).

(which was very well present in the monomer) and clearly implies the formation of Si–Si main chain in the poly(methyl vinylsilane). $-\text{CH}=\text{CH}_2$ usually shows peaks at $985\text{--}995\text{ cm}^{-1}$ and $905\text{--}915\text{ cm}^{-1}$ which is absent in this spectrum, and implies that vinyl group is reacted in this procedure and polysilanes with the saturated substituents may be obtained as the polymer product [20,35–37]. FTIR spectra of co-polymers of poly(methylvinylsilane-co-ferrocene) has Si–CH₃ (815 cm^{-1} and 1261 cm^{-1}), Si–CH (1105 cm^{-1}), C–H bending (2963 cm^{-1}) groups. Since FTIR spectrum of the dicyclo pentadienyl groups absorb at 1611 cm^{-1} and 1658 cm^{-1} [38], the peak for the cyclopentadienyl ring

in the above polymer was observed near 1636 cm^{-1} , which implies that the polymer contain Si–Fe bond in their backbone. FTIR spectra of polysilane doped with titanocene and zirconocene have also been obtained and their spectral results are given in Appendix A.

¹H NMR spectra (Fig. 3) of poly(methyl vinylsilane) has three major peaks near δ 0.056, 1.0 and 1.53 ppm, these chemical shifts predicted for the above polymer (Si–CH₃, methyl proton and Si–CH–CH₂–). The results of ¹H NMR are consistent with this prediction. Since ¹H NMR chemical shifts for catenated silicon atoms with methyl substituents can be observed in the range of δ 0–0.4 ppm [7], the peak observed near δ 0.056 ppm is assigned to Si–CH₃ group. The observed peak near δ 1.0 is assigned to methyl proton. The characteristic chemical shift for Si–vinyl moiety usually shows their peak at δ 5.6–6.2 ppm with a characteristic-coupling pattern, which is absent in this spectrum, and it implies that the vinyl groups reacted in the procedure, and polysilane is obtained with saturated substituents [34,39,40].

¹H NMR spectra of copolymers of polysilane doped with ferrocene, titanocene and zirconocene have also been obtained and the results are presented in Appendix A.

By the functionalization of polysilane with various metallocenes, the fluorescence property is being enhanced when compared with conventional polysilanes, and thus functionalized polysilane have more fluorescence effect. This has been achieved by the co-polymerisation of polysilane with metallocenes [41]. The emission spectra of poly(methyl vinylsilane) shows the emission at 450 nm which corresponds to $\sigma\text{--}\sigma^*$ transition shown in Fig. 4a. This may be due to the presence of Si–Si sigma bond and the spectrum (Fig. 4b), which does not exhibit, the emission property, it may be due to less probability of formation of Si–Fe bond in the polymer backbone. The poly(methyl vinylsilane) with metallocene units will attract much attention as $\sigma\text{--}\pi$ conjugated organosilicon polymers, which have feasible application as electroluminescent material because this polysilane will be regarded as semiconductors with high photoluminescence quantum efficiency [42]. The spectrum (Fig. 4c and d) clearly shows the emission of polysilane around 455 nm and 451 nm when doped with titanocene and zirconocene respectively. In the case of co-polymer of polysilane doped with zirconocene, the result suggests that the energy transfer occurred from Si–Si sigma bond to cyclopentadienyl ring in the excited state.

3.2. X-ray diffraction analysis

The X-ray powder diffraction pattern of poly(methyl vinylsilane), poly(methyl vinylsilane-co-ferrocene), poly(methyl vinylsilane-co-titanocene) and poly(methyl vinylsilane-co-zirconocene) are shown in Fig. 5a–d. These profiles clearly indicate that the polymers are crystalline in nature. It indicates that the polymerisation step

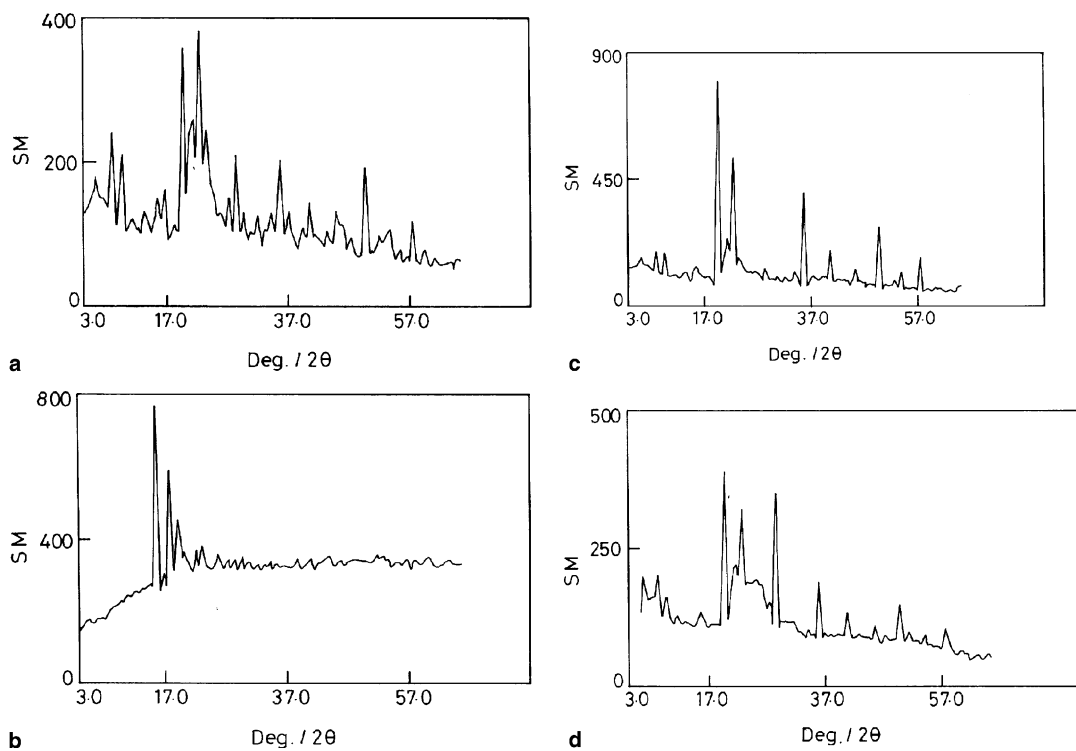


Fig. 5. XRD spectra of (a) poly(methyl vinylsilane), (b) poly(methyl vinylsilane) co-polymer with ferrocene, (c) poly(methyl vinylsilane) co-polymer with titanocene and (d) poly(methyl vinylsilane) co-polymer with zirconocene.

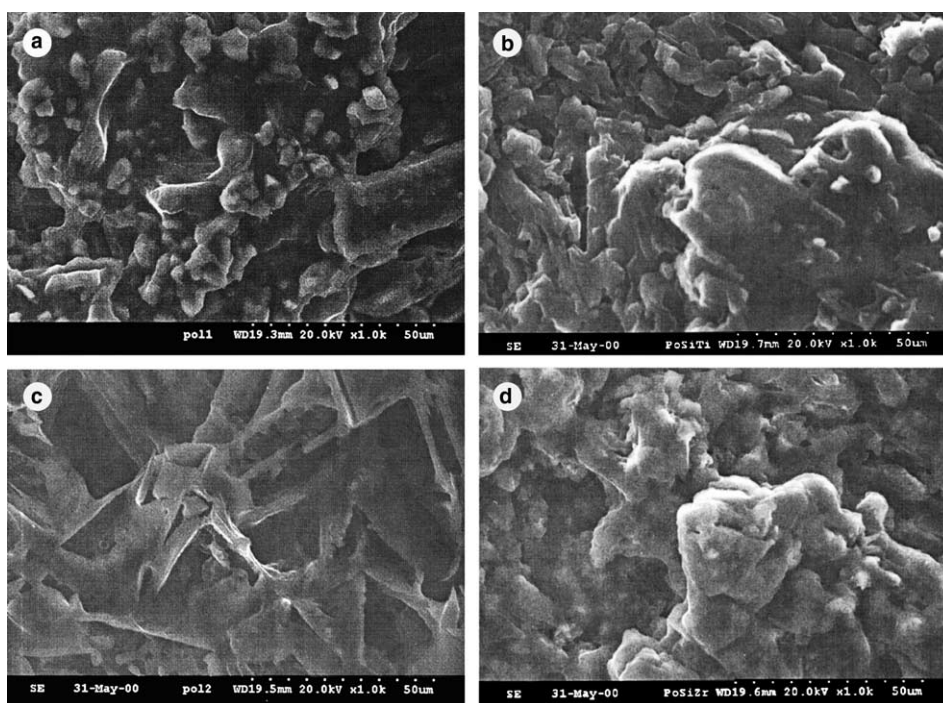


Fig. 6. SEM micrograph of (a) poly(methyl vinylsilane), (b) poly(methyl vinylsilane) co-polymer with ferrocene, (c) poly(methyl vinylsilane) co-polymer with titanocene and (d) poly(methyl vinylsilane) co-polymer with zirconocene.

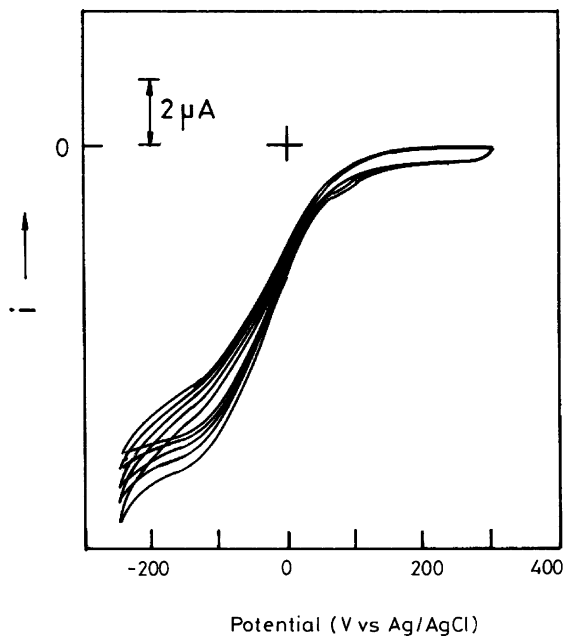


Fig. 7. CV response of 0.1 M poly(methyl vinylsilane) in 0.2 M tetrabutylammonium tetrafluoroborate in DME at Au electrode. Sweep rate: 25 mV/s.

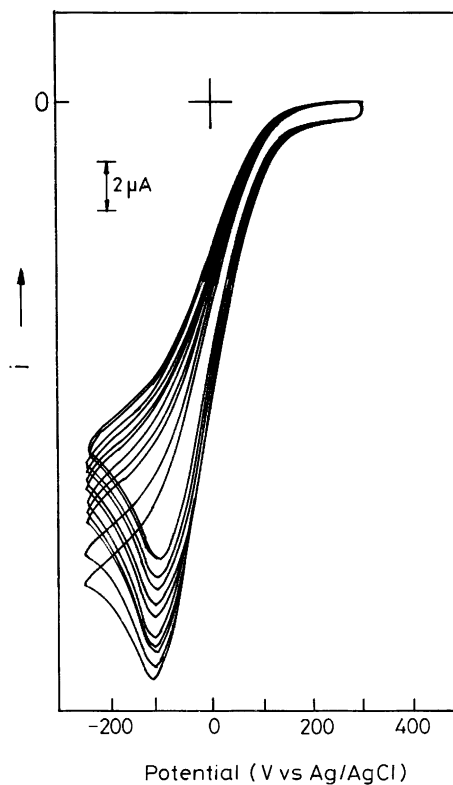


Fig. 9. CV response of 0.1 M poly(methyl vinylsilane) + 0.08 M titanocene di chloride in 0.2 M tetrabutylammonium tetrafluoroborate in DME at Au electrode. Sweep rate: 25 mV/s.

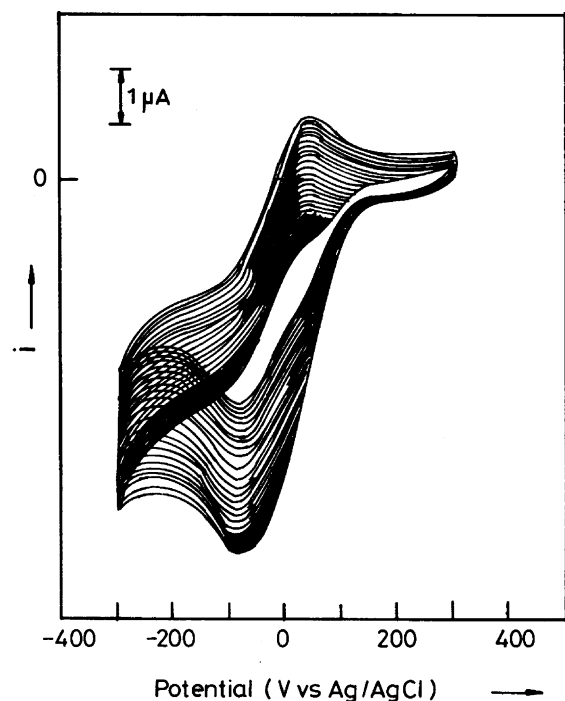


Fig. 8. CV response of 0.1 M poly(methyl vinylsilane) + 0.08 M ferrocene in 0.2 M tetrabutylammonium tetrafluoroborate in DME at Au electrode. Sweep rate: 25 mV/s.

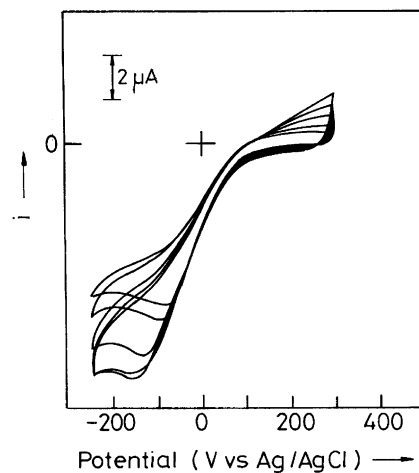


Fig. 10. CV response of 0.1 M poly(methyl vinylsilane) + 0.08 M zirconocene di chloride in 0.2 M tetrabutylammonium tetrafluoroborate in DME at Au electrode. Sweep rate: 25 mV/s.

under constant current electrolysis in non-aqueous media is very slow and forming in regular fashion. The crystallinity is increased as the polymer is doped with

Table 2
Current response of dichloro methyl vinylsilane and with different dopants at different sweep rates

Sweep rate (mV s ⁻¹)	Cathodic peak current (μA)			
	Silane	Ferrocene	Titanocene	Zirconocene
25	9.8	5.0	16.2	24.0
50	10.6	6.0	18.2	24.4
75	19.0	6.6	19.4	27.0
100	20.2	7.8	20.4	30.2
150	20.8	9.2	21.0	31.2

titanocene and zirconocene but the crystallinity is disappeared when it is doped with ferrocene [43,44].

3.3. Scanning electron microscopic analysis

SEM micrographs of poly(methyl vinylsilane), poly(methyl vinylsilane-co-ferrocene), poly(methyl vinylsilane-co-titanocene) and poly(methyl vinylsilane-co-zirconocene) films which were cast from THF solution are shown in Fig. 6a–d. It is very clear from the micrographs that except ferrocene co-polymer, all other polymers show nearly uniform crystalline particles on the surface and the poly(methyl vinylsilane-co-ferrocene) show amorphous nature. This phenomenon has been confirmed by XRD data [45,46] as well.

3.4. Cyclic voltammetry

In order to check the mechanism of formation of polymers, the cyclic voltammetric studies were carried out at the gold electrode surface. Ag/Ag⁺ was used as the quasi-reference electrode and platinum electrode as the counter electrode. To determine the reliability of the chosen three electrode system, the well-known voltammogram of ferrocene was recorded and the oxidation as well as the reduction peaks (0.5 and 0.1 V vs SCE) was in complete agreement with the literature values [6]. Fig. 7 shows the typical irreversible voltammetric behavior of 0.1 M dichloro methyl vinylsilane at Au electrode surface and it is clear from the figure that at -150 mV vs Ag/Ag⁺, the irreversible reduction of silane is taking place [47]. Since the reduction potential of silane in this polymerisation at -150 mV vs Ag/Ag⁺, is very much higher than the polymerisation of vinyl group which is at -1.0 V vs Ag/Ag⁺, the lower current density is preferred for the electro-reductive bulk polymerisation, this avoids the polymerisation through vinyl group [48]. It is also inferred that the polymer gets deposited and grows on the electrode surface as the time increases during the potential scanning. This is in accordance with the continuous cycling shown in Fig. 7 indicating an increase in peak current with the number of cycles. And it

is also found that the peak current increases with sweep rate. From the potential of formation of polysilane (-150 mV vs Ag/Ag⁺), it can be understood that ability to take electron is more for silane molecule and the polysilane forms through radical formation [4,49].

The effect of dopants on the cyclic voltammetric response of silane reduction is compared in Figs. 8–10 for ferrocene, dicyclo pentadienyl titanium dichloride and dicyclo pentadienyl zirconium dichloride respectively. It is seen from the figures that except for response from ferrocene (Fig. 8), the other two-voltammetric responses (Figs. 9 and 10) are very much similar to dichloro methyl vinylsilane voltammetric response (Fig. 7) showing similar mechanism. So it is clear that as in Si-Si, Si-Ge-Si-Ge here also Si-M-Si-M (M = Ti or Zr) bonds are formed [4]. But in the case of ferrocene addition (Fig. 8), the irreversible peak become reversible may be due to different mechanism for the formation [47]. This may be due to the easily removable chloride ions present in dicyclo pentadienyl titanium dichloride and dicyclo pentadienyl zirconium dichloride as in the case of dichloro methyl vinylsilane and it is absent in ferrocene moiety. The peak current response for different dopants is presented in Table 2 and it can be seen that as the sweep rate increases the cathodic peak current also increases. It is clearly indicating that the metal doped onto the matrix of the polysilane is only responsible for the increase in the current response. The linear increase in the peak current with respect to sweep rate indicates that the formation of polymer is under diffusion control.

3.5. Summary

(1) A very efficient and reproducible electrochemical method was employed to synthesis the polysilane materials. (2) This method gave higher molecular weight polymers without using ultrasound, which is often necessary in the Wurtz type coupling reaction. (3) The formation of Si-Si catenation achieved by the electrochemical reduction of organo chlorosilanes. (4) The formation of Si-Fe, Si-Ti and Si-Zr bonds have also been achieved by a similar method of approach using aluminum electrodes. (5) The polymers were well characterised using UV, FTIR and NMR spectral techniques. (6) The molecular weight of the polymers can be controlled by the concentration of the monomer. (7) Polymers obtained have good opto-electronic properties.

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Appendix A

Poly(methyl vinylsilane-co-titanocene) shows its characteristic infrared absorption (KBr): Si-CH₃ (882 cm⁻¹) [39], Si-CH (1105 cm⁻¹), C-H bending (2962 cm⁻¹), cyclo pentadienyl ring (cp) (1654 cm⁻¹) [35–37].

Poly(methyl vinylsilane-co-zirconocene) shows its characteristic infrared absorption (KBr): Si-CH₃ (883 cm⁻¹), Si-CH (1105 cm⁻¹), C-H bending (2961 cm⁻¹) cyclo pentadienyl ring (cp) (1652 cm⁻¹) [35–37].

In the above polymers the absence of Ti-Cl (821 cm⁻¹) and Zr-Cl (814 cm⁻¹) in FTIR spectra indicates that the formation of silicon-metal bonds such as Si-Ti and Si-Zr respectively [50,21].

The ¹H NMR spectrum of the poly(methyl vinylsilane-co-ferrocene) shows characteristic chemical shifts (CDCl₃) at δ 0.238 ppm (s, 6 H, Si-CH₃), δ 1.2 ppm (s, 3H, methyl proton) and δ 4.25 ppm is due to the presence of cyclo pentadienyl ring (s, 4H, cp) in the polymer backbone [30,51–54].

The ¹H NMR spectrum of the poly(methyl vinylsilane-co-titanocene) shows characteristic chemical shifts (CDCl₃) at δ 0.23 ppm (s, 6H, Si-CH₃), δ 1.2 ppm (s, 3H, methyl proton) and δ 3.56 ppm is due to the presence of cyclo pentadienyl ring (s, 5H, cp) in the polymer backbone [30,51–55]. Here, the cyclo pentadienyl ring with titanium metal atom causes the signals to be shifted to upfield.

The ¹H NMR spectrum of the poly(methyl vinylsilane-co-zirconocene) shows characteristic chemical shifts (CDCl₃) at δ 0.22 ppm (s, 6 H, Si-CH₃), δ 1.4 ppm (s, 3H, methyl proton) and δ 4.89 ppm is due to the presence of cyclo pentadienyl ring (s, 5H, cp) in the polymer backbone [30,39,51–55]. Here, the cyclo pentadienyl ring with zirconocene metal atom causes the signals to be shifted to down field.

In all the spectrum of Si-metalocenes copolymers, the peaks at δ 5.6–6.2 ppm for Si-vinyl moiety is completely absent, which clearly implies that, the copolymers also not contain vinyl group in their backbone as in the case of homo-polymer.

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