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Articles

High Molecular Weight Poly(ferrocenediyl–silanes): Synthesis and Electrochemistry of $[-(C_5H_4)Fe(C_5H_4)SiR_2-]_n$, R = Me, Et, *n*-Bu, *n*-Hex

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High molecular weight poly(dialkylsilane–ferrocenediyls) of general formula $[-(C_5H_4)Fe(C_5H_4)SiR_2-]_n$, R = methyl, ethyl, butyl, and hexyl) were synthesized by thermal polymerization of the corresponding [1]-(dialkylsilyl)ferrocenophane. The polymers are stable up to 450–500 °C and with the smaller alkyl groups, e.g., methyl and butyl, the polymers are predominantly crystalline in the solid state. The voltammograms of these polymers in Et_4NBF_4/dichloromethane show two reversible redox peaks for the stepwise oxidation of the polymer where half of the ferrocene centers on the polymer chain (possibly alternating) are oxidized in the first reaction and the remaining in the second reaction. Both oxidation states of the polymers are stable to the electrochemical conditions. The redox potentials of both reactions are affected by the size of the alkyl group. Although, these polymers are soluble in dichloromethane, they deposit on the electrode surface and influence the shape of the voltammograms by affecting the diffusion of the electrolyte ions to the electrode. The polymers were chemically oxidized with anhydrous $FeCl_3$. Two equivalents of $FeCl_3$/(ferrocene) are required to fully oxidize the polymers.

Introduction

The study of organometallic and inorganic polymers has become an area of considerable interest since such systems can be useful precursors to novel materials unavailable from other source.[1,2] In our laboratories we have an interest in the incorporation of transition metals into such polymers with particular interest in silicon-containing materials. Ferrocene has been well-known to display an unique reversible redox reaction in organic solutions and research has focused on the synthesis of polymeric materials containing ferrocene both as a component of the backbone or as pendant groups. Examples are poly(ferrocenylene persulfide),[3] poly(vinylferrocene),[4] and poly((*m*-aminoanilino)methylferrocene).[5] Such polymers have been used in modified electrodes,[6] electrochemical sensors,[7] and nonlinear optical devices.[8] We reported that incorporation of pendant ferrocene into poly(silane) resulted in materials with enhanced photochemical stability and for the first time produced poly(silane) with reversible redox behavior.[9] As an extension of this study we recently reported that thermal treatment of [1]-(dialkylsilyl)ferrocenophane led to linear polymeric systems.[10] The Manners group independently also reported on these new polymers and noted briefly that they exhibited two reversible redox events resulting from oxidaton of alternating ferrocene units.[11] A related phosphorus polymer was synthesized by anionic polymerization of P-bridged

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Table I. General Characteristics of [1]-(Dialkylsilyl)ferrocenophanes Used as Monomers

R	yield, %	bp (mp) °C	UVλ_{max}, nm	NMR (δ, ppm, C_6D_6)		
				^1H	^{13}C	^{29}Si
Me	68	(78–79)	477	4.66[a] (C_5H_4) 4.20[a] (C_5H_4) 0.62 (CH_3)	77.69 (C_5H_4) 75.58 (C_5H_4) 32.32 (C_5H_4, C–Si) −3.29 (Me)	−4.62
Et	83	(103–104)	479	4.41[a] (C_5H_4) 3.98[a] (C_5H_4) 1.20–1.86 (m, C_2H_5)	77.69 (C_5H_4) 75.58 (C_5H_4) 32.60 (C_5H_4, C–Si) 6.69, 3.34 (Et)	1.53
n-Bu	34	$138^{0.005}$	478	4.40[a] (C_5H_4) 3.99[a] (C_5H_4) 1.60–0.95 (m, C_4H_9)	77.50 (C_5H_4) 75.89 (C_5H_4) 32.63 (C_5H_4, C–Si) 26.49, 25.78 14.06, 11.60 (Bu)	−1.45
n-Hex	3	$169^{0.005}$	479	4.42[a] (C_5H_4) 4.09[a] (C_5H_4) 1.34–0.87 (m, C_6H_{13})	76.93 (C_5H_4) 75.32 (C_5H_4) 32.67 (C_5H_4, C–Si) 33.58, 33.00 23.04, 22.56 13.78, 11.37 (Hex)	−1.47

[a] 4H, dd, J = 1.6 Hz, C_5H_4.

Table II. Molecular Weights (M_w), Melting Temperatures (T_m), Decomposition Temperatures (T_d), and Nuclear Magnetic Resonance (NMR) Results of Poly(dialkylsilane–ferrocenediyls)

polymers	M_w[a]	T_m (°C)	T_d (°C)[b]	NMR (δ, ppm in C_6D_6)		
				^1H	^{13}C	^{29}Si
Poly(PCSiMe$_2$)	144 200	122	478	4.55(4H, bd s); 4.15 (4H, bd s); 0.61 (6H, bd s)	73.75; 71.99; 71.66; −0.53	−6.25
Poly(FCSiEt$_2$)	27 100	91	455	4.32 (4H, bd s); 4.15 (4H, bd s); 1.29–1.05 (10H, m)	74.06; 71.83; 70.04; 8.50; 6.472.49	
Poly(FCSiBu$_2$)	374 000	134	500	4.37 (4H, bd s); 4.21 (4H, bd s); 1.70–1.02 (18H, m)	74.19; 71.95; 70.70; 27.40; 27.17; 14.93; 14.21	−4.82
Poly(FCSiHex$_2$)	193 800			4.64 (4H, bd s); 4.49 (4H, bd s); 1.96–1.24 (26H, m)	74.12; 71.88; 70.61; 34.25; 32.18; 24.98; 23.17; 15.31; 14.47	−4.88

[a] M_w was determined by GPC in THF using poly(styrene) standards. [b] T_m and T_d were determined by DSC and TGA.

ferrocenophane by Seyferth et al. in 1982.[12] In this paper, we report the synthesis and electrochemistry of poly(ferrocenediyl–silanes) with methyl, ethyl, *n*-butyl, and *n*-hexyl groups (poly(FCSiR$_2$)).

Experimental Section

Synthetic Procedures. All reactions and other manipulations were performed in dry, oxygen-free, solvents in an atmosphere of argon or in vacuo using standard Schlenk techniques. Chlorosilanes were purchased from Huls American Inc., and *n*-butyllithium, TMEDA, and ferrocene were obtained from Aldrich Chemicals. Dilithioferrocene was obtained by literature procedures[13] as a yellow crystalline powder, washed twice with hexane, and used without any further characterization. The monomers, [1]-(dialkylsilyl)ferrocenophanes, were prepared using the same procedures as in ref 14. Yields and characteristics of the monomers are given in Table I. Typical syntheses of the polymers are as follows:

(a) *Poly(dimethylsilane–ferrocenediyl) (poly(FCSiMe$_2$))*: 1.0 g (4.12 mmol) of [1]-(dimethylsilyl)ferrocenophane was sealed in vacuo in a pyrex tube, 1 × 6 cm, and heated at 125 °C for 6 h. The reaction product, an amorphous glass solid, was dissolved in benzene and precipitated from hexane. The precipitate was filtered and dried in vacuum. This procedure gave 0.65 g (65%) of poly(FCSiMe$_2$). The polymer was characterized by ^1H, ^{13}C, and ^{29}Si NMR and UV spectroscopy, and all the data are recorded in Table II. A similar procedure can also be used for synthesis of polymers with the ethyl, *n*-butyl, and *n*-hexyl groups.

(b) *Poly(dibutylsilane–ferrocenediyl) (poly(FCSiBu$_2$))*: A solution of 3.4 g (16 mmol) of $(n\text{-}C_4H_9)_2SiCl_2$ in 10 mL of hexane was added very slowly to a slurry of 14 mmol of dilithioferrocene in 20 mL of hexane and stirred overnight. The reaction mixture was filtered and solvent was removed in vacuo. The distillation of the resulting liquid, 138 °C/0.05 mm Hg gave 1.78 g of liquid fraction that solidified slowly at room temperature after distillation, [1]-di-*n*-butylsilylferroceneophane (yield 34%), and a glassy, solid dark red residue. The residue was washed twice with hexane and dissolved in benzene, and the polymeric product was precipitated from hexane. The polymeric product was filtered and vacuum dried to yield 0.8 g (18%). The molecular weights, spectroscopic data, and thermal characteristics of the polymers are recorded in Table II.

Thermal Analysis. The DSC scans were run using a Perkin-Elmer DSC-7 in dry nitrogen for the polymers with the methyl and *n*-butyl groups or in dry helium for the polymer with the *n*-hexyl groups and using a heating rate of 10 °C/min. The TGA analyses were run using a Perkin-Elmer TGS-2.

Wide-Angle X-ray Scattering (WAXS). The films were cast from benzene solutions onto precleaned petrographic slides and dried in vacuum. X-ray powder diffraction patterns were obtained on a Scintag XDS 2000 diffractometer using a nickel filtered Cu Kα radiation at scanning rates of 0.5–2°/min.

Electrochemistry. Dichloromethane and tetraethylammonium tetrafluoroborate, Et_4NBF_4, were purchased from EM Science and used without further purification. The electrochemical measurements were carried out in a one-compartment cell equipped with a platinum disk working electrode (surface area = 0.2 cm^2), a gold wire counter electrode, and an Ag/AgCl (3.8 N KCl) double-junction reference electrode. The cyclic voltammograms were recorded using a EG&G PAR potentiostat/galvanostat (Model 273) connected with a IBM *x*–*y*–*t* plotter (Model 7424 MT). Dichloromethane solutions containing 0.1 M Et_4NBF_4 and 0.1 mM polymer were used for measurements. The chronocoulometry experiments were performed on the solution containing 1.0 mM polymer by stepping the potentials from 0.00 to 0.65 V (the first oxidation reaction) and from 0.00 to 1.00 V (the overall oxidation reaction), and recorded the charge with time. The electrochemical cell was kept at the initial potential for 1 min to achieve equilibrium. The chronocoloumetric response

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of the 0.1 M Et_4NBF_4 in dichloromethane solution with no polymer was used to correct for the double-layer charging on the working electrode.

Chemical Oxidation. The chemical oxidation of the poly(ferrocenediyl–silanes) in dichloromethane solutions was performed by adding portions of an anhydrous $FeCl_3$/dichloromethane solution. The final polymer concentration was kept at 3.40 mM. The chemical oxidation was followed with the UV–visible spectra of the solutions in a quartz cell recorded using a HP diode array spectrophotometer (Model HP 8452A).

Results and Discussion

Synthesis of Polymers. Synthesis of the poly(dialkylsilane–ferrocenediyl) was readily accomplished as noted in the Experimental Section; however, there are a few aspects of the preparation that merit discussion. In the case of poly($FCSiMe_2$) synthesis via isolation and purification of the [1]-(dimethylsilyl)ferrocenophane was the initial route used. In the case of poly($FCSiBu_2$) and poly($FCSiHex_2$), such a process could also be used except that purification of the complex was more difficult. We therefore preferred to produce the polymers in situ, i.e., treatment of the dilithioferrocene with dialkyldichlorosilane at ambient temperature followed by filtering off salts, removal of solvent, and heating the residual material to the appropriate temperature. Recovery of the polymers by precipitation worked well for all the systems, and we found that the yields and molecular weights of the resulting polymers were not appreciable different using this technique.

Polymer Morphology. The WAXS spectra of these polymers in the solid state indicate structural ordering in the polymers with the methyl, ethyl, and *n*-butyl side groups. Figure 1a,b illustrates the predominate ordered and crystalline nature of the polymers with the methyl and *n*-butyl groups. There is very little amorphous background in these diffractograms unlike the completely amorphous character of the *n*-hexyl analog (Figure 1c). Indeed, the polymer with the *n*-hexyl groups is elastomeric and may be drawn into very fine silken threads. Further inspection of the data shows that the regularity of the crystalline materials, poly($FCSiMe_2$) and poly($FCSiBu_2$), have significantly different spacings, increasing from the smaller methyl group (maximum spacing 6.34 Å) to *n*-butyl (maximum spacing 11.06 Å). Given the absence of any crystallinity for the *n*-hexyl polymer, it is clear that the increasing length of the side chains play a dominant role in the structure of the polymers. This conclusion is reinforced by the DSC data. The polymers with the methyl and n-butyl groups exhibit melting transitions in the range 123–133 °C, whereas the *n*-hexyl polymer exhibits no events beyond a low temperature T_g at −22 °C as befits an amorphous material. As we reported for the dimethyl polymer,[15] all three polymers are stable to heating and show initial weight loss with heating at 450–500 °C (see Table II). Overall the data illustrate that the size of the alkyl groups dramatically alters the morphology of the polymers. Similar property variations have been noted for polysilanes, $(R_2Si)_n$.[16,17] To study this in detail, we are presently engaged in the synthesis of oligomeric model systems and indeed recently reported the synthesis, electrochemistry, and single-crystal structure of $FcSiMe_2(C_5H_4)Fe(C_5H_4)SiMe_2Fc$.[18]

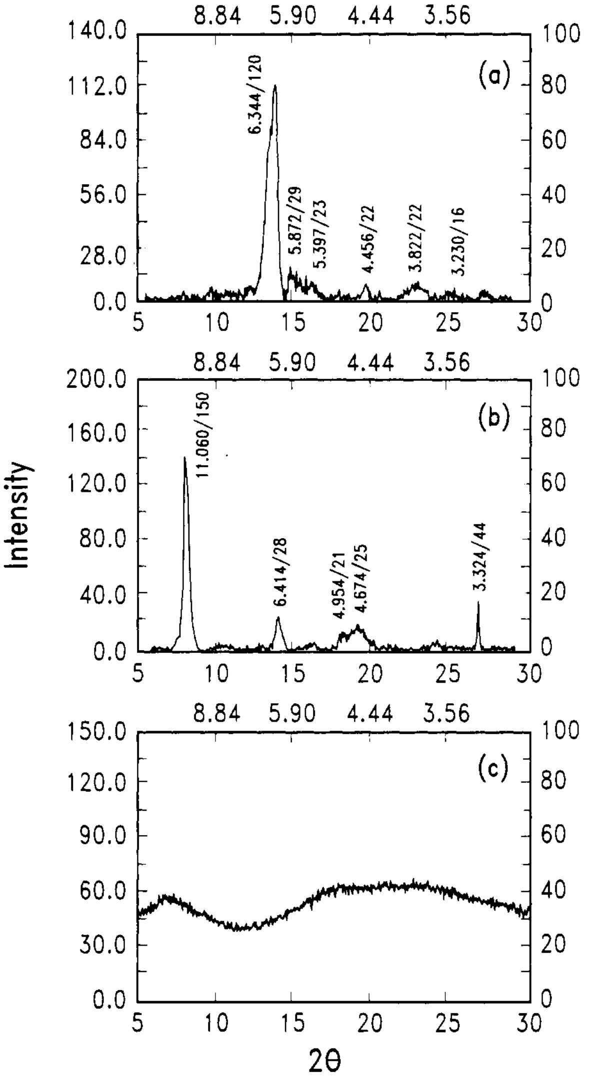

Figure 1. WAXS diffractograms of (a) poly($FCSiMe_2$), (b) poly($FCSiBu_2$), and (c) poly($FCSiHex_2$).

Cyclic Voltammetry. The electrochemical behavior of poly(dialkylsilane–ferrocenediyls) dissolved in dichloromethane containing 0.1 M Et_4NBF_4 was studied by cyclic voltammetry. The cyclic voltammogram of a 0.1 mM poly($FCSiBu_2$) solution at different scanning rates are shown in Figure 2. Two reversible redox peaks appear with E_{pa} values at 0.48 and 0.82 V vs Ag/AgCl (3.8 M KCl). This result is similar to the brief report for poly($FCSiMe_2$) by Foucher et al.[11] and for poly(ferrocenediyl–persulfide) by Brandt et al.[3] The two peaks have been proposed to result from the stepwise oxidation of the polymer where the alternating ferrocene centers along the chain are oxidized in the first reaction (Scheme I). This separation must reflect charge polarization of the neighboring ferrocene centers in the polymer both through the SiR_2 groups[19] and through space. The separation of the oxidation potentials is also observed with the molecular analogs of similar structure. For example, $FcSiMe_2Fc$ shows two

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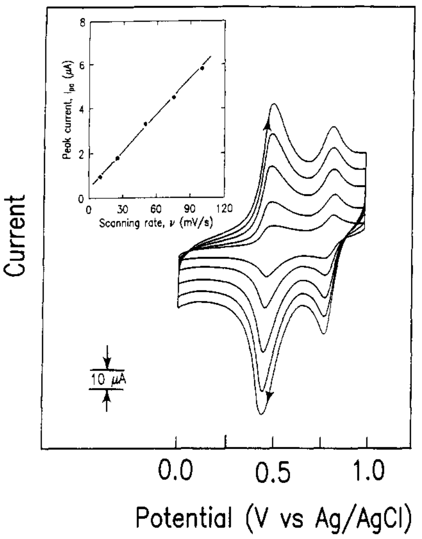
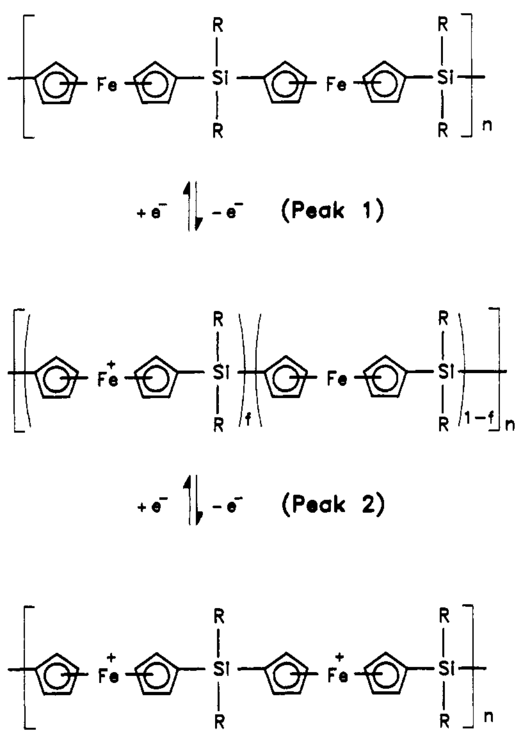


Figure 2. Cyclic voltammograms at different scanning rates of 0.1 mM poly(dibutylsilane–ferrocenediyl) in CH_2Cl_2 solution containing 0.1 M Et_4NBF_4. Inlay: plot of I_{Da} vs ν.

Scheme I



reversible, closely overlapping peaks with E_{pa} at 0.58 and 0.73 V.[20] The oxidation of these polymers behaves differently from the polymers with pendent ferrocene groups, i.e., poly(vinylferrocene)[4] and poly(ferrocenemethyl-*co*-phenylmethylsilane),[9] which display only one reversible redox couple. In addition, the ferrocene groups behave like discrete redox centers and do not display the cooperative behavior observed with poly(vinylferrocene).[4]

Poly($FCSiBu_2$) is stable to the electrochemical conditions and the voltammograms are reproduced with repeated cycling. Of particular interest is the fact that the peaks appear symmetrical and the anodic-cathodic peak separations are ca. 40 mV. In addition, I_{pa1} and I_{pa2} scale linearly with the scan rates between 10 and 100 mV/s. The plot for the first peak is shown in the inlay and has a slope of 5.4×10^{-5} A/(V/s). The slope for the second peak could not be measured accurately because the base line is not well defined. This current response suggests adsorption of the polymer on the electrode surface,[21] and although unexpected since the polymer is soluble, this behavior has been observed with other polymers.[4]

The fraction of ferrocene units oxidized in the first peak (f) and second peak ($1 - f$; see Scheme I) can be obtained from the relative areas, since $n = 1$ for the oxidation of each ferrocene unit. Although this measurement is difficult because the peaks overlap, the relative peak sizes were found to vary with the scan rate, where, f is 0.58, 0.64, 0.71, 0.73, and 0.78 for the 10, 25, 50, 75, and 100 mV/s scan rates. The problem of the relative peak sizes is not unique to the polymer and is also seen in the voltammogram for $FcSiMe_2Fc$,[20] where the first–second peak ratio is 60–40. Only with biferrocene are the peaks sufficiently separated to confirm the equal areas.[20]

The slope in Figure 2 provides $\Gamma = 0.8 \times 10^{-10}$ mol/cm^2 using the average value of 0.7 for f in Anson's equation,[21], i.e., $I_{pa} = (n^2F^2\Gamma\nu)/(4RT)$, where n, F, ν, R, and T are the electrochemical stoichiometry, Faraday constant, scan rate, gas constant, and absolute temperature, respectively. This value corresponds ca. 0.1 of a monolayer of active molecular species.[6] Considering the conformational encumberance associated with the polymer, this could be a monolayer of polymer chains. Since the polymer (M_w = 374 000) has ca. 2000 units, this corresponds to a Γ of 0.4×10^{-13} (mol of polymer)/cm^2 or 400 000 Å^2/(polymer chain). This corresponds to a spherical footprint with a radius of 360 Å. For comparison, a polymer solid with this molecular weight packed into a sphere would have a radius of ca. 90 Å (using a density of 1 g/cm^3). Therefore, the polymer localized on the electrode surface is fairly swollen.

With a 1 mM poly($FCSiBu_2$) solution, the two waves have very different forms. The peak at 0.5 V is very broad and flat, making it difficult to discertain the peak maximum. The signal resembles the step wave observed for those cases involving slow diffusion across a permeable membrane on the electrode.[22] The second peak at 0.9 V is again sharp. The two reduction peaks produced in the reverse scan are well defined, symmetrical peaks (Figure 2b). With this concentration of polymer, the peak heights scale with $\nu^{1/2}$. This change in response compared with the 0.1 mM polymer solution probably reflects a shift in the kinetics to the slow diffusion of the electrolyte ion across a thicker, less porous polymer film on the electrode. In line with this proposal, we find that with 0.1 M Bu_4NOTs electrolyte the oxidation waves for poly($FCSiBu_2$) are broad and poorly defined. The shape of the waves are very sensitive to the scan rate and quickly become more distorted at the higher rates. With 0.1 M Bu_4NBF_4 electrolyte the voltammogram closely resembles the one with 0.1 M Et_4NBF_4 electrolyte. Therefore, the oxidation reaction appears to be particularly sensitive to the diffusion of the electrolyte anion to the electrode.

Similar voltammograms were obtained with 0.1 mM poly($FCSiMe_2$) and poly($FCSiEt_2$) in dichloromethane, and the results are summarized in Table II. The fraction of the charge in the first peak, f, is 0.52 with both polymers.

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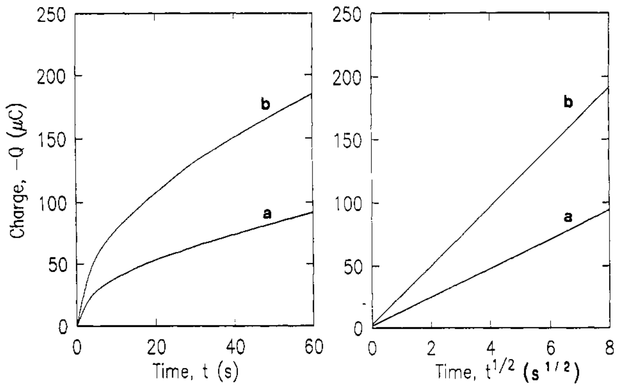

Figure 3. Plots of charge, Q vs t, and Q vs $t^{1/2}$ of 1.0 mM poly(dibutylsilane–ferocenediyl) in CH_2Cl_2 solution containing 0.1 M ET_4NBF_4 for potential steps from 0.00 to (a) 0.65 and (b) 1.00 V.

With poly($FCSiMe_2$) there is a small increase in f with scan rate (up to 0.6 at 100 mV/s), while with poly($FCSiEt_2$) the values have 5% random scatter. The peak currents, I_{pa1} and I_{pa2} of poly($FCSiMe_2$) and poly($FCSiEt_2$) scale linearly with the scan rate. For poly($FCSiMe_2$) the slope of the I_{pa1}–ν plot is 3.2×10^{-5} A/(V/s) and Γ is ca. 0.6×10^{-10} mol/cm^2 using $f = 0.5$. For poly($FCSiEt_2$) the slope is 5×10^{-5} A/(V/s) and Γ is ca. 1×10^{-10} mol/cm^2 ($f = 0.5$). The voltammogram for poly($FCSiHex_2$) is very different showing a single broad peak between 0.4 and 0.9 V and the maximum at 0.8 V. With these polymers, the first oxidation peak shifts to less anodic potentials as the alkyl groups size increases from methyl (0.54 V) to butyl (0.48 V), probably due to an inductive effect. The second oxidation peak shifts anodically. These polymers are assumed to prefer a conformation in which the Fe atoms are pseudo-trans along the polymer chain as proposed for the diferrocenylalkanes.[23] The anodic shift in the second peak may reflect distortions of the pseudo-trans conformations due to the alkyl groups which reduces the distance between ferrocene centers and enhances their interaction.

Chronocoulometry. The chronocoulometry response with poly($FCSiMe_2$), poly($FCSiEt_2$), and poly($FCSiBu_2$) shows a linear charge, Q, vs $t^{1/2}$ dependence. This can be seen in Figure 3, which shows Q response for both the first and the two combined reactions for a 1.0 mM poly($FCSiBu_2$) solution. The corresponding slopes are 10×10^{-6} and 18×10^{-6} C/s$^{1/2}$, respectively. D was estimated for the first oxidation reaction using f in the Cottrell equation for linear diffusion at a planar electrode, i.e., $D = 2nFAC(Dt/\pi)^{1/2}$, where A and C are the surface area of the electrode and the initial polymer contentration.[24] As mentioned above, this measures the diffusion of the electrolyte ions across the polymer film on the electrode. Using $(f)C = 0.6$ mM ferrocene centers, $D = 5 \times 10^{-7}$ cm^2/s is estimated. As seen in Table III, the D values decrease as the size of the alkyl group increases, possibly reflecting the relative encumberance to the segmental motion of the polymer chain and the diffusion of the ions. Simply for comparison, the diffusion coefficient for 1.0 mM poly(vinylferrocene) in dichloromethane is 4.5×10^{-6} cm^2/s and for ferrocene it is 17.6×10^{-6} cm^2/s. These values were obtained under similar conditions.

Table III. E_{pa} and D Values for the Oxidation of Poly(dialkylsilane–ferrocenediyls)

polymer[a]	E_{pa1} (V)	E_{pa2} (V)	$10^7 D_1$ (cm^2/s)	f[b]
poly($FCSiMe_2$)	0.50	0.72	10	0.52
poly($FCSiEt_2$0	0.51	0.76	6	0.52
poly($FCSiBu_2$)	0.48	0.82	5	0.58–0.78
poly($FCSiHex_2$)	ca. 0.80			
$FcSiMe_2Fc$[c]	0.58	0.73		0.6
FcFc[c]	0.46	0.80		0.5
ferrocene	0.60		176	

[a] 0.1 mM and 1 mM polymer solutions were used for the E_p and D determinations, respectively. [b] Fraction of polymer oxidized in the first wave. [c] Reference 20.

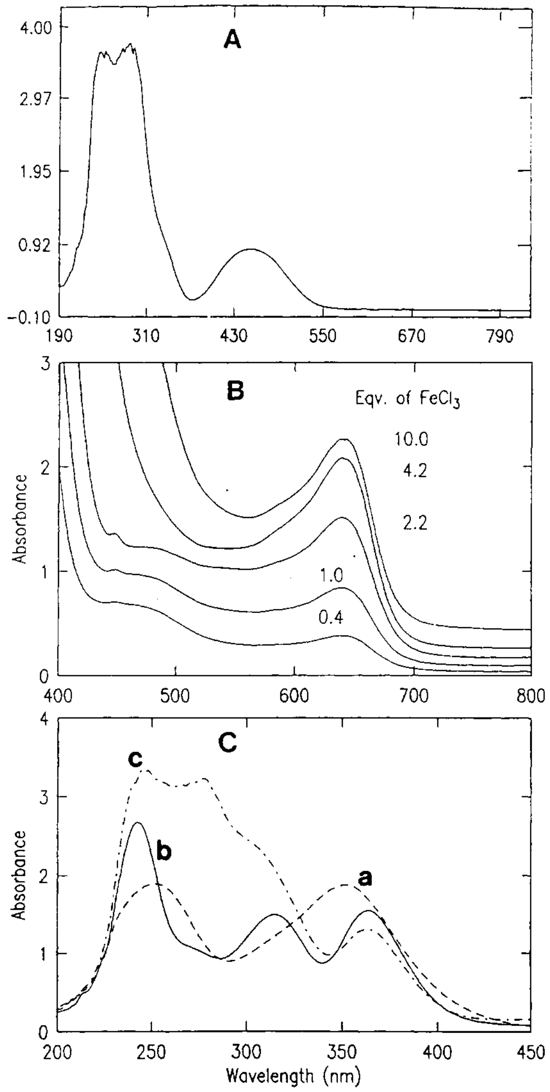

Figure 4. UV–visible spectra of CH_2Cl_2 solution containing (A) neutral poly(dibutylsilane–ferrocenediyl), (B) oxidized poly(dibutylsilane–ferrocenediyl) with different amount of $FeCl_3$ added and (C) (a) oxidized poly(dibutylsilane–ferrocenediyl), (b) $FeCl_2$, and (c) $FeCl_3$.

UV–Visible Spectroscopy and Chemical Oxidation. The UV–visible spectrum of the neutral poly($FCSiBu_2$) in dichloromethane solution is shown in Figure 4a. This solution has a clear yellow color and exhibits two main absorption bands in the spectrum. The strong band at 280 nm probably corresponds to the $\pi \rightarrow \pi^*$ transition of the cyclopentadiene rings.[25] The relatively weak bands

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at 452 nm belongs to the symmetry-forbidden transitions of electrons from nonbonding a_{1g} to the antibonding e_{1g}^* level of the iron 3d- orbital which is particularly sensitive to the substituents and interaction between the ferrocene units.[26] However, this band is not affected by the size of the alkyl substituent since the poly($FCSiMe_2$) and poly($FCSiEt_2$) solutions also show a weak band at 452 nm.

The poly(dialkylsilane–ferrocenediyls) are easily oxidized using anhydrous $FeCl_3$ in dichloromethane solution. The reaction occurs spontaneously as indicated by the rapid color changes from clear yellow to green and then blue depending on the amounts of $FeCl_3$ added and the solutions are stable for several days. The UV–visible spectra of the oxidized poly($FCSiBu_2$) in dichloromethane solutions are shown in Figure 4b. The band at 452 nm disappeared and a new band appeared at 642 nm which probably corresponds to the symmetry-allowed $^2E_{2g} \rightarrow {}^2E_{1u}$ transition of the ferrocenium cations.[27] Like the neutral form, this band is not affected by the alkyl substituents. The intensity of the $^2E_{2g} \rightarrow {}^2E_{1u}$ absorption band increased with the amount of $FeCl_3$ added, and this was used to determine the stoichiometry of the chemical oxidation of these polymers. It is known that $FeCl_3$ will oxidize conjugated polymers with a stoichiometry of $2FeCl_3$ per cation produced.[28] Hence, the equation for the stepwise oxidation of poly($FCSiR_2$) is shown below where FC and FC^+ are the ferrocene and ferrocenium centers:

$$(FCSiR_2FCSiR_2) + 2FeCl_3 \rightarrow (FC^+SiR_2FCSiR_2) + FeCl_4^- + FeCl_2$$

$$(FC^+SiR_2FCSiR_2) + 2FeCl_3 \rightarrow (FC^+SiR_2FC^+SiR_2) + FeCl_4^- + FeCl_2$$

Our results are consistent with the stoichiometry. As seen in Figure 5 the intensity of the ferrocenium cation absorption band at 642 nm (corrected for the background at 750 nm) increases linearly with added $FeCl_3$ to a saturation level with 4 equiv of $FeCl_3$/(FC dimer unit), or 2 equiv of $FeCl_3$/FC. The $FeCl_2$ produced from the reaction is identified by the appearance of a shoulder and an absorption band at 316 and 362 nm as seen in Figure 4C which shows the UV–visible spectra of $FeCl_3$, $FeCl_2$, and oxidized poly($FCSiBu_2$). These results agree with the results previously reported for the chemical oxidation of thiophene oligomers and polymers which required 4 equiv of $FeCl_3$/dication.[29,30]

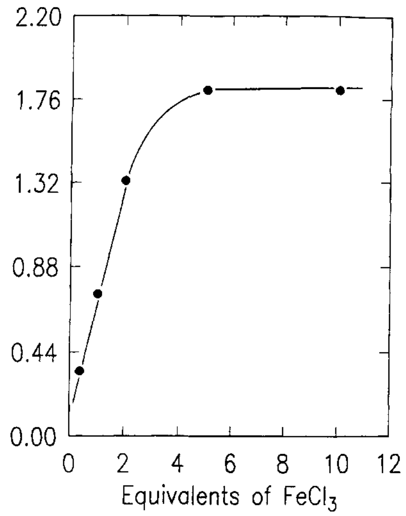

Figure 5. Plot of absorbance ($A_{642\ nm} - A_{750\ nm}$) of poly(dibutylsilane–ferrocenediyl) vs. the equivalents of $FeCl_3$ added based on $(FCSiR_2FCSiR_2)_n$.

Conclusion

The poly($FCSiR_2$) polymers in this study have some crystalline structure in the solid state and are thermally stable up to 450–500 °C. In solution, they are easily oxidized and the cyclic voltammograms for these polymers in dichloromethane show two reversible redox reactions between 0.5 and 0.8 V. The position of the first and second oxidation peaks shifts monotonically with the size of the alkyl group. Although, the poly(dialkylsilane–ferrocenediyls) are soluble in dichloromethane, they deposit on the electrode surface as indicated by the linear dependence of I_{pa} on scan rate. Poly($FCSiR_2$) polymers can be chemically oxidized by anhydrous $FeCl_3$, with a stoichiometry of 2 equiv of $FeCl_3$/(ferrocene unit).

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