Electrochemical and Electrochromic Properties of Poly(dialkylsilyleneferrocenylene) Films

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Thin films of poly(dialkylsilyleneferrocenylene) (poly(FCSiR$_2$), R = methyl, ethyl, *n*-butyl, and *n*-hexyl) were coated onto a platinum electrode, and their electrochemical behavior was measured while immersed in either an aqueous or organic electrolyte. The cyclic voltammograms of the films do not show the sharp symmetrical peaks expected for surface localized reactions. Instead, in 0.1 M aqueous H_2SO_4 there is one unsymmetrical oxidation peak with a sharp current rise indicating that the neutral films are poorly solvated and they become solvated when the break-in voltage of 0.54 V is reached. In the cathodic scan, the reduction peak is small and broad. In 0.1 M Et_4NBF_4/CH_3CN two redox couples are observed as was previously reported for these polymers in solution. In this electrolyte, the lack of chemical reversibility in the redox reaction of the film is observed. The films are electrochromic and change color from clear yellow (neutral) to light green (oxidized) when the applied potential is changed from 0.0 to 1.0 V. The oxidation peak potentials shift with the size of the alkyl substituents on the polymer.

Introduction

Polymers containing ferrocene in the backbone or as pendant groups have received a great deal of research attention because of the potential applications in modified electrodes,[1] electrochemical sensors,[2–4] and nonlinear optical devices.[5] Recently, high molecular weight dialkylsilane–ferrocenylene polymers with different alkyl groups have been prepared by thermal ring-opening polymerization.[6–9] Poly(alkylferrocenylsilyleneferrocenylene) polymers were also successfully synthesized in the same manner.[10] The cyclic voltammograms of the dialkylsilane ferrocenylene polymers in dichloromethane solution are complicated and show the stepwise oxidation of the polymer.[6,7] In addition, the polymer deposits on the electrode as it becomes oxidized, and this affects the kinetics of the oxidation process. In this paper, we report the electrochemistry of dialkylsilane ferrocenylene polymers when cast as films on the electrode and immersed in aqueous and acetonitrile electrolytes. The electrochromic properties of these polymer films were also investigated (Scheme 1).

Experimental Section

Chemicals and solvents were obtained from Aldrich Chemical and used as received. The dialkylsilane polymers were synthesized by the procedures outlined in our previous studies,[6] and the particular M_w and M_n properties of the samples used in this study were: $[FC(SiR_2)]_n$, R = Me, M_w = 144 000, M_n = 103 000; R = Et, M_w = 27 100, M_n = 22 500; R = *n*-Bu, M_w = 374 000, M_n = 233 000; R = *n*-Hex, M_w = 194 000, M_n = 81 000. Polymer films with the thickness of 280–420 nm on platinum foil electrodes (0.70 cm^2) were obtained by casting from the tetrahydrofuran–polymer solutions. The electrochemical measurements of poly(dialkylsilyleneferrocenylene) films were performed in a one-compartment cell equipped with a gold wire counter electrode and an Ag/AgCl (3.8 N KCl) double-junction reference electrode. The cyclic voltammograms were recorded using an EG&G potentiostat/galvanostat (Model 273) and an IBM *x*–*y*–*t* plotter (Model 7424 MT). For the in situ UV–visible spectral measurements, the polymer films were cast on 2.5 cm by 2.5 cm area NESA glass. The resulting films were coherent, smooth and had a very even thickness. The UV–visible measurements were made using a diode array HP 8452A spectrophotometer.

Results and Discussion

The electrochemical behavior of poly(dialkylsilyleneferrocenylene) films in aqueous and organic electrolytes was studied by cyclic voltammetry. The voltammograms do not show the sharp symmetrical oxidation–reduction peaks expected for an electrode-localized electroactive film. Instead, as seen in the cyclic voltammograms for a poly(FCSiMe$_2$) film in 0.1 M aqueous H_2SO_4 (Figure 1), there is one unsymmetrical oxidation peak at 0.62 V with a sharp rise in the current at 0.54 V. The neutral films must be

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(1) Murray, R. W. *Electroanal. Chem.* **1983**, *13*, 246.

(2) Hale, P. D.; Inagaki, T.; Karan, H. I.; Okamoto, Y.; Skotheim, T. A. *J. Am. Chem. Soc.* **1989**, *111*, 3482.

(3) Hillman, A. R.; Taylor, D. A.; Hammett, A,; Higgins, S. J. *J. Electroanal. Chem.* **1989**, *94*, 423.

(4) Frew, J. E.; Hill, H. A. O. *Anal. Chem.* **1987**, *59*, 933.

(5) Wright, M. E.; Svejda, S. A. In *Materials for Nonlinear Optics: Chemical Perspectives*, Marker, S. R., Sohn, J. E., Stucky, G. D., Eds.; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991; p 603.

(6) Nguyen, M. T.; Diaz, A. F.; Dement'ev, V. V.; Pannell, K. H. *Chem. Mater.* **1993**, *10*, 1389.

(7) Nguyen, M. T.; Diaz, A. F.; Dement'ev, V. V.; Sharma, H.; Pannell, K. H. IS&T Symposium on Electric Imaging Science and Technology, San Jose, CA, Jan 1993, Paper 1910–28; SPIE Proc. **1993**, *1910*, 230.

(8) Foucher, D. A.; Tang, B. Z.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246.

(9) (a) Tang, B. Z.; Foucher, D. A.; Lough, A.; Coombs, N.; Manners, I. *Macromolecules* **1993**, 523. (b) Manners, I. *Angew. Chem.*, **Int. Ed. Engl. 1993**, 1709.

(10) Dement'ev, V. V.; Cervantes-Lee, F.; Nguyen, M. T.; Diaz, A.; Pannell, K. *Organometallics*, submitted.

0897-4756/94/2806-0952$04.50/0

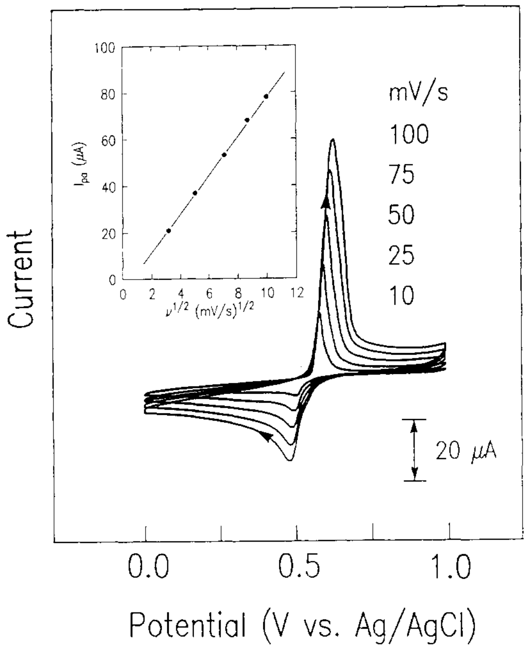
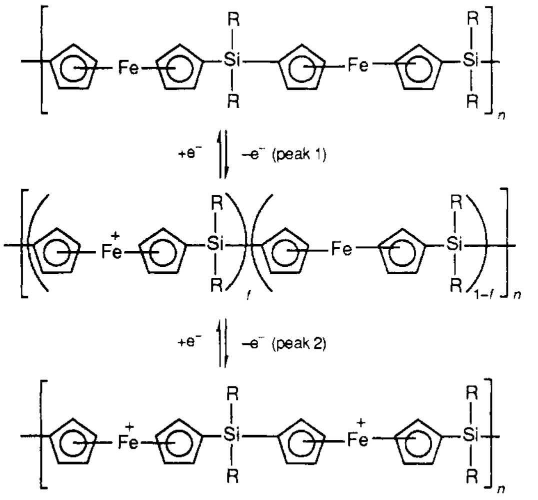


Figure 1. Cyclic voltammogram of a poly(dimethylsilyleneferrocenylene) film immersed in aqueous 0.1 M H_2SO_4.

Scheme 1. Dialkylsilane Ferrocenylene Polymers: R = Methyl, Ethyl, *n*-Butyl, and *n*-Hexyl



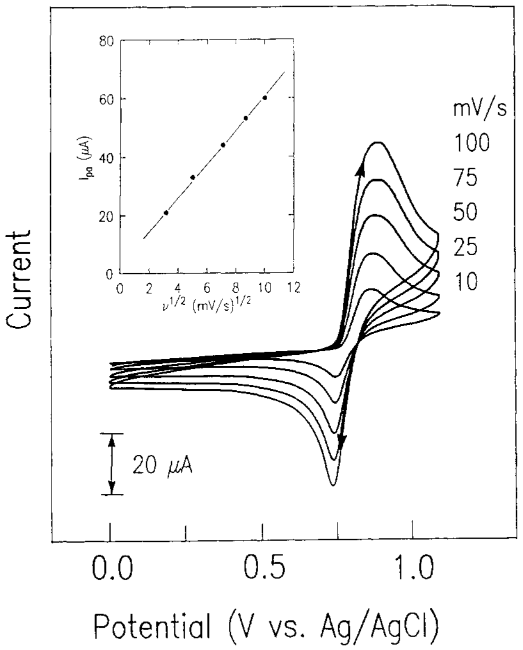


Figure 2. Cyclic voltammogram of a poly(dihexylsilyleneferrocenylene) film immersed in aqueous 0.1 M H_2SO_4.

Table 1. Oxidation Potentials of Poly(dialkylsilyleneferrocenylene) Films on Platinum from Cyclic Voltammetry Recorded at 100 mV/s[a]

poly(dialkylsilylene-ferrocenylene)	E_{bp}/V	E_{pa1}/V	E_{pa2}/V
Films Immersed in 0.1 M H_2SO_4			
dimethyl	0.54	0.62	
diethyl	0.63	0.71	
dibutyl	0.68	0.79	
dihexyl	0.75	0.91	
Films Immersed in 0.1 M Et_4NBF_4/CH_3CN			
dimethyl		0.52	0.71
diethyl		0.57	0.74
dibutyl		0.59	0.75
dihexyl		0.64	0.76

[a] E_{bp}, break-in potential; E_{pa}, oxidation peak potential.

poorly solvated and highly resistive and are not oxidized until the break-in potential (E_{bp}) is reached and the electrolyte penetrates the film. The peak maxima are artificial and the oxidation peaks (E_{pa}) must lie closer to the position of the cathodic peak (E_{pc}) which appears at 0.48 V. The cathodic peak is smaller and has a long current decay reflecting the slow diffusion of ions and solvent out of the reduced polymer film. The peak current, I_{pa}, increases linearly with $\nu^{1/2}$ (inlay of Figure 1) supporting the interpretation that the reaction rate is limited by the diffusion of the electrolyte into the polymer film. The electrooxidation of the dialkylsilane ferrocenylene polymers in solution was shown to involve the interconversion of neutral ferrocene and ferrocenium cations,[6,7] and the same process must be involved with these films. Similar results were observed for polyvinylferrocene films.[11,12] The films are not completely stable to the redox process and the voltammograms show a ca. 10% reduction in the size of the peaks after 20 scanning cycles at 100 mV/s. Films coated on a quartz microbalance indicate that there is no corresponding weight loss after this cycling period [13]. Thus, the reduction in the peak size must reflect a loss in electroactivity and not loss of material off the electrode.

The polymers with the larger alkyl substituents have a greater stability to the redox process. For example, the di-*n*-butyl polymer shows ca. 5% reduction in the size of the peaks after 20 cycles. With these polymers, the redox peaks are broader and a break-in voltage is always observed. The voltammogram for the poly(FCSiHex$_2$) film is shown in Figure 2. The peak positions for the various polymers are listed in Table 1, and the small differences are probably due to differences in the film resistivities and permeabilities. We reported previously that the dry films of the dialkylsilane ferrocenylene polymers with methyl, ethyl, and *n*-butyl groups have partial crystalline character while the polymer with the *n*-hexyl groups is a glassy amorphous elastomer.[6] This morphology change may also affect the response of the polymer films.

In 0.1 M Et_4NBF_4 acetonitrile electrolyte the films exhibit two redox couples as was observed with the polymers dissolved in dichloromethane.[6,7] As seen in Figure 3 with both the poly(FCSiMe$_2$) and poly(FCSiHex$_2$)

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(11) Daum, P.; Murray, R. W. *J. Electroanal. Chem.* **1979**, *103*, 289.

(12) Daum, P.; Murray, R. W. *J. Phys. Chem.* **1981**, *85*, 389.

(13) Nguyen, M. T.; Borges, G. L.; Kanazawa, K. K.; Diaz, A. F.; Dement'ev, V. V.; Pannell, K. H. Presented at the 207nd American Chemical Society Meeting, San Diego, CA, Mar 1994. Abst PMSE 0011.

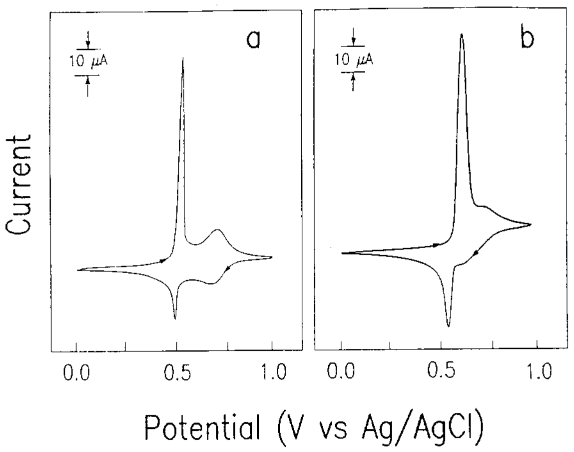

Figure 3. Cyclic voltammograms of a (a) poly(dimethylsilyleneferrocenylene) and (b) poly(dihexylsilyleneferrocenylene) films immersed in 0.1 M $TEABF_4/CH_3CN$. Scan rate: 100 mV/s.

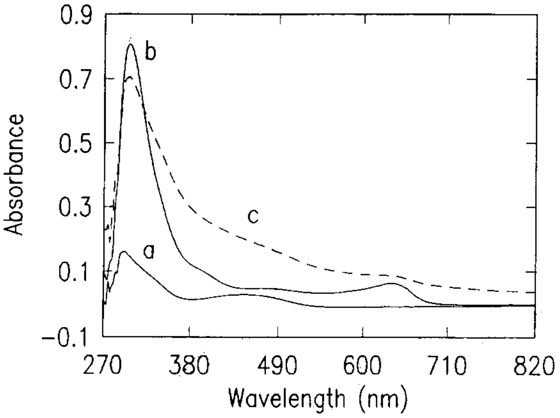

Figure 4. UV-visible spectra of a poly(dihexylsilyleneferrocenylene) film immersed in aqueous 0.1 M H_2SO_4. Spectra measured at (a) 0.0, (b) 1.0, and (c) 0.0 V (after the film was oxidized at 1.0 V).

films the first redox couple is very sharp, as expected for a surface localized redox process, and the second redox couple is relatively broad, possibly reflecting solvent swelling after the first oxidation. The cathodic peak in the reverse scan reaction could not be determined because the oxidized form of the polymer slowly dissolved off the electrode. The polymer in solution was detected in the UV-visible spectrum of the electrolyte solution recovered from the electrochemical analysis. Again the oxidation peaks shift anodic with the large alkyl groups on the polymer, probably reflecting an increased resistivity of the film. The cyclic voltammograms of these polymers dissoved in CH_2Cl_2 shows symmetrical peaks and the i_p values scale linearly with the scan rate suggesting that the polymers are localized on the electrode and there is no diffusion.[6,7] The first oxidation peak shifts cathodically and the second peak shifts anodically with increasing alkyl group size. This result was explained in terms of the steric effect on the polymer chain conformation.[6,7,14]

The poly(dialkylsilyleneferrocenylene) films are electrochromic, and color changes from light yellow to light green are observed during the potential sweep cycle. The spectral changes accompanying this color change were measured on films cast on a transparent Nesa glass electrode. As seen in Figure 4, the in situ UV-visible spectrum of a poly($FCSiHex_2$) film immersed in 0.1 M H_2SO_4 solution shows two absorption bands when the potential is at 0.0 V (clear yellow film). The 292-nm band is assigned to the *π–π transition* of the cyclopentadiene rings (curve a), and the weak bands at 452 nm to the symmetry-forbidden nonbonding a_{1g} to the antibonding $e_{1g}{}^*$ transition of the Fe 3d orbital.[6] Upon increasing the applied potential to 1.0 V, the color of the film slowly changes to light green, the 452-nm band disappears, the 292-nm band increases, and a new band apepars at 646 nm (curve b). The new band was assigned to the symmetry-allowed transitions associated with the ferrocenium species.[14] The color changes occur slowly with both these large NESA electrodes and the small platinum electrodes, even though the films were only 20 nm thick. The color change occurred during 5–10 min. The spectrum for the poly($FCSiHex_2$) film did not return completely to its original form when the potential was returned to 0.0 V (curve c) due to some chemical degradation of the polymer. From both the visual inspection of the weak color change in the film and the spectra in Figure 4, it is clear that the optical contrast ratio in the visible region is too small for practical electrochromic device applications. The electrochromic and spectral responses were similar for the other poly(dialkylsilyleneferrocenylene) films.

In contrast with these results, 100–200-nm-thick films of polyaniline can be switched between the neutral and the oxidized state in aqueous H_2SO_4 electrolyte with a time constant of 0.1 ms.[15] The films are electrochromic and change color from light yellow to blue-black with an optical contrast ratio in the visible spectrum of 2.[15] Even a 20-nm-thick film of polyvinylferrocene can be switched between the neutral and oxidized forms within 1 ms. The oxidation–reduction rates of these films are known to be limited by the diffusion of ions in and out of the film. Therefore, the slower rates observed with the dialkylsilane–ferrocenylene polymer films is probably related to the poor compatibility between these polymers and the electrolyte. This will result in slow ion diffusion into the film and a slow redox process.

In summary, films of poly(dialkylsilyleneferrocenylene) on NESA glass can be electrochemically oxidized and reduced in aqueous and CH_3CN electrolytes. The neutral films are quite resistive and a break-in voltage is seen in the aqueous electrolyte. The redox kinetics are slow and depend on the transport of electrolyte ions in the films. The films are electrochromic and slowly change color from yellow (0.0 V) to green (1.0 V) when the polymer is oxidized. These results demonstrate that the new class of polymers with a ferrocenylene unit incorporated into the backbone have interesting electrochromic properties, however, caution must be excercised with respect to the claims of technological utility that have recently appeared.[16] Given the poor response times and reversibility exhibited by the films, major structural modifications of the materials will be needed to approach the properties which can be used in a practical device.

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(14) Gorton, J. E.; Lentzner, H. L.; Watts, W. E. *Tetrahedron* **1977**, *49*, 1589.

(15) LaCroix, J. C.; Kanazawa, K. K. Diaz, A. F. *J. Electrochem. Soc.* **1989**, *136*, 1308.

(16) Degani, R. *Chem. Eng. News*, **1993**, *Aug 2*, 23.