

Electrochemical Behaviors of Poly(ferrocenylsilane) Solutions

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ABSTRACT: The electrochemical behaviors of two kinds of poly(ferrocenylsilanes) (PFS) with different substituent groups in CH₂Cl₂ solutions were investigated by means of cyclic voltammetry (CV) and electrochemical quartz crystal microbalance. The results demonstrated that the CV processes of the PFS on the glass carbon electrode surface in CH₂Cl₂ solutions are the diffusion-controlled reversible processes. The oxidative state of PFS forms an adsorption layer on the electrode surface during the oxidation process. The interaction of active ferrocene centers along the main chain induces the stepwise redox process, and makes the

CV waves of the PFS solutions present two couples of peaks. The diffusion coefficients of PFS in CH₂Cl₂ solution are much larger than those of PFS in films. The different electrochemical behaviors of the two PFS solutions indicated that the molecular structure of polymer has influence on the electrochemical properties of the PFS. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 789–794, 2007

Key words: poly(ferrocenylsilane) (PFS); solution; electrochemistry; cyclic voltammetry (CV); electrochemical quartz crystal microbalance (EQCM)

INTRODUCTION

The high molecular weight organometallic polymers with ferrocene sites in the main chain are a kind of novel functional polymer materials.^{1–3} A great deal of research attention has been focused on these new materials in the past decade because of their electric, optical, and magnetic activities. These special polymers have extensive potential applications and can be used as electrochemical sensors,^{4,5} electrochromic and thermochromic material,⁶ protective charge dissipation coating,⁷ magnetic polymer, and magnetic ceramic precursors.^{8–11} The electrochemical studies on this kind of polymer are an important foundation to application due to these sensors being used in electrochemical environments. In previous articles,^{12–14} we have reported that various supporting electrolytes, electrolyte concentration, temperature, and solvents have noticeable influences on the electrochemical behavior of poly(ferrocenylsilane) (PFS) films in

aqueous and various organic solutions. In this article, we report the cyclic voltammetry (CV) behaviors of two kinds of PFS CH₂Cl₂ solutions. The mass changes of the electrode surface during the CV processes in these PFS solutions are measured using the electrochemical quartz crystal microbalance (EQCM). The two PFS have different substituents with various steric and electronic effect. The mechanism of the electrochemical process and the influence of molecular structure on the electrochemical behavior of PFS solutions are discussed.

EXPERIMENTAL SECTION

Structure of PFS

The two kinds of poly(ferrocenylsilane) (PFS) investigated were polyferrocenyldimethylsilane (PFDMS) and polyferrocenylmethylphenylsilane (PFMPS); their structures are shown in Scheme 1. These PFS polymers were synthesized in our laboratory, their structures were characterized by H NMR and FTIR, and their molecular weights and polydispersity index (PDI = M_w/M_n) were measured by GPC.¹³ For the resultant PFDMS, the weight-average molecular weight (M_w) was 1.14×10^5 g/mol, the number-average molecular weight (M_n) was 2.51×10^5 g/mol, and the PDI was 4.54. The corresponding data of the resultant PFMPS were $M_w = 1.12 \times 10^5$ g/mol, $M_n = 4.96 \times 10^5$ g/mol, and PDI = 2.26.

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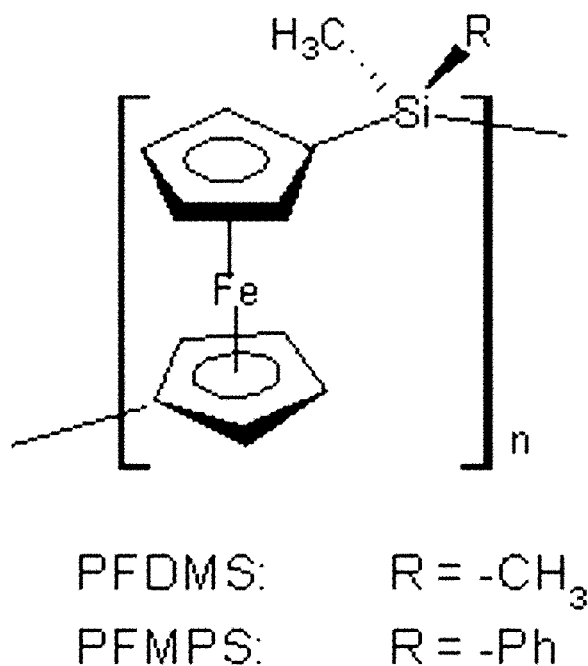
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Scheme 1 Structure of PFS.

Instruments and reagents

The CV measurements were carried out with a CHI-630A electrochemical analyzer (CH Instruments, Austin, TX), in an undivided three-electrode cell. All electrodes were from CH Instruments. A platinum wire counter electrode and an Ag wire reference electrode were used. The working electrode was a Teflon-shrouded glassy carbon disk electrode (0.3 cm diameter, 0.071 cm² geometric area). The electrode potentials in this article were relative to the Ag wire reference electrode. The glass carbon electrode surface was hand-polished to a mirror finish before it was used with 0.05 μm Al₂O₃ paste on felt, washed by ultrasonic cleaner in double-distilled water. The Ag wire electrode was cleaned by dipping in 1M nitric acid for 10 s, then rinsed by double-distilled water before it was used. The working electrode was preoxidized for 2 s at 1.2 V before every CV scan.

The EQCM measurements were carried out with a CHI-400A electrochemical quartz crystal microbalance (CH Instruments, Austin, TX). A quartz crystal plate with gold electrodes (0.5 cm diameter) sprayed on either sides served as working electrode. The surface area of gold electrode was 0.196 cm². The appa-

rent oscillation frequency of the AT-cut quartz crystal was 7.99 MHz. The system calibration constant was obtained as 0.739 Hz/ng, that is, the mass change was 1.35 ng for 1-Hz frequency change. The gold film quartz electrode surface was washed before it was used with H₂SO₄ : 30% H₂O₂ (v/v = 3 : 1), double-distilled water, and ethanol.

All solvents and chemical reagents were purchased from commercial sources. They all were of analytical- or pure-grades and used without further purification. The water was double-distilled. Dichloromethane (CH₂Cl₂) solution containing 0.10M Et₄NBF₄ and 1.0 mM polymer (based on the monomer units) were used for measurements. The reason for the selection of CH₂Cl₂ is that CH₂Cl₂ is an excellent solvent for these PFS polymers, in which solution the stable and repeatable CV waves could be obtained. The electrochemical measurements were carried out at 25°C.

iR drop compensation

As the ohmic potential (*iR*) drops of organic solutions are considerable, especially in less-polar solutions, the *iR* drops of the solutions were measured and auto-compensated with CHI instruments in the electrochemical measurements.

RESULTS AND DISCUSSION

CV behaviors of two PFS CH₂Cl₂ solutions

The electrochemical behaviors of two PFS CH₂Cl₂ solutions were studied by cyclic voltammetry (CV). The CV peak potential (*E_p*) data of two PFS CH₂Cl₂ solutions are listed in Table I, and the CV waves of two PFS CH₂Cl₂ solutions at different scan rates are exhibited in Figure 1.

The CV waves of two PFS CH₂Cl₂ solutions, as shown in Figure 1, present two couples of redox peaks. These CV waves are different from the cases of ferrocene¹⁵ and some hanging type ferrocene-based polymers in which the ferrocene units appended on main chains as pendant groups, i.e., poly(vinylferrocenes).¹⁶ The CV waves of ferrocene solution and those hanging type ferrocene-based polymer solutions all display one reversible redox couple. Because the Fe atoms of PFS exist in the same chemical environment in their molecules, the

TABLE I
The CV Peak Potential Data of Two PFS CH₂Cl₂ Solutions^a

Polymer solution	<i>E_{pa1}</i> (V)	<i>E_{pc1}</i> (V)	<i>E₁^{0'}</i> (V)	Δ <i>E_{p1}</i> (V)	<i>E_{pa2}</i> (V)	<i>E_{pc2}</i> (V)	<i>E₂^{0'}</i> (V)	Δ <i>E_{p2}</i> (V)	Δ <i>E^{0'}</i> (V)
PFDMS	0.619	0.584	0.602	0.035	0.775	0.755	0.765	0.020	0.163
PFMPS	0.677	0.614	0.646	0.063	0.858	0.818	0.838	0.040	0.192

^a PFS concentration: 1.0 mM (in Fe sites); electrolyte: 0.10M Et₄NBF₄; scan rates: 0.10 V/s; temperature: 25°C. Φ 3 mm glass carbon disk electrode.

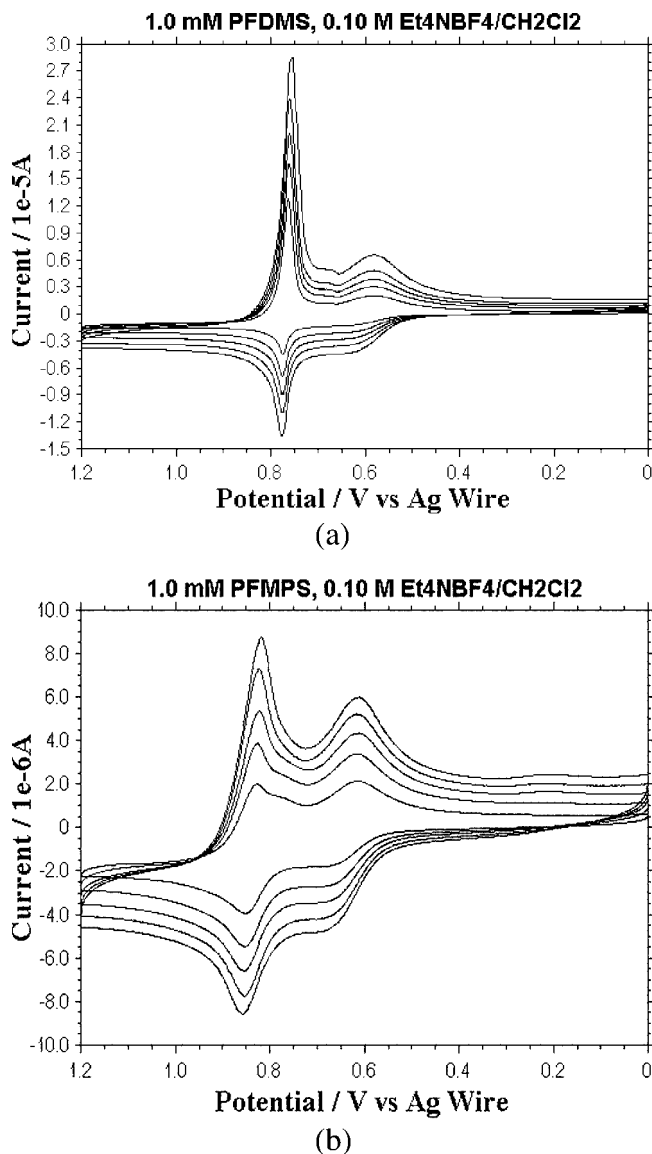


Figure 1 Cyclic voltammograms of two PFS CH_2Cl_2 solutions at different scan rates: (a) PFDMS and (b) PFMPs. PFS concentration: 1.0 mM (in Fe sites), electrolyte concentration: 0.10M Et_4NBF_4 ; temperature: 25°C; scan rates: from inside to outside 20, 40, 60, 80, 100 mV/s. Φ 3 mm glass carbon disk electrode.

double-peak phenomena of the PFS solutions were suggested as a stepwise oxidation mechanism,^{6,17} in which process the initial oxidation occurred at alternating ferrocene sites because of the strong electrochemical interaction between the active iron atoms along the PFS main chain, and that subsequent oxidation of the remaining iron(II) centers was energetically less favorable and, therefore, occurred at a higher potential, and so two oxidation waves were obtained.

Comparing CV waves of PFDMS CH_2Cl_2 solutions in Figure 1 with the corresponding CV waves of PFDMS films in aqueous and organic solutions,^{12,14} we can find that the CV peak widths of PFDMS

CH_2Cl_2 solutions are very narrow, the peak–peak separations ΔE_p ($\Delta E_p = E_{pa} - E_{pc}$, where E_{pa} is the potential of oxidation peak and E_{pc} is the potential of reduction peak) are very small, smaller than 60 mV, and the peak potentials do not change with increasing potential scan rate v . These CV features indicate that the diffusion rates of PFDMS in CH_2Cl_2 solutions and the rates of electrode reaction of PFDMS CH_2Cl_2 solutions are fast, and the redox processes of PFDMS CH_2Cl_2 solutions are reversible electrochemical processes.

We notice that the reduction currents i_{pc} of two PFS solutions are slightly larger than their oxidation currents i_{pa} , as shown in Figure 1. The reason may be that the oxidative state of PFS, poly(ferrocenium) cations have low solubility in CH_2Cl_2 solutions, which make the poly(ferrocenium) separate from the solution and be adsorbed on the electrode surface to form an adsorption layer. This poly(ferrocenium) adsorption layer on the electrode surface would lead to higher concentration of ferrocene sites on the electrode surface and form larger i_{pc} . This conclusion has been reinforced by EQCM measurements. The CV waves of two PFS CH_2Cl_2 solutions are all closed and repeated curves in CV scan, it means that the oxidation state of PFS forming an adsorption layer and the reduction state dissolving into solution are reversible.

To confirm the PFS adsorbed on electrode surface, the preoxidized electrode that was oxidized for 5 s at 1.2 V oxidation potential in PFS CH_2Cl_2 solutions was took out and parked into 0.1M Et_4NBF_4 CH_2Cl_2 solution (blank solution) to play CV reduction scan, and the CV reduction wave of PFS was obtained.

As seen in the CV waves of two PFS solutions in Figure 1, the two couples of redox peaks have different forms. The first couple of redox peaks at low potential are broad and flat, it may imply a slow diffusion across solution on the electrode redox process. The second couple of peaks at high potential are relatively sharp, it possibly just reflects an adsorption layer formed and surface localized redox process after the first oxidation.

There are distinguishable differences in the CV waves of the two PFS solutions, as shown in Figure 1. We can notice that the CV waves of PFMPs exhibit the smaller CV i_p , the broader peak width, the more positive peak potential E_p , and the larger peak–peak separation ΔE_p . It means that the molecular structure of the polymer has a noticeable influence on the electrochemical process. Apparently, the phenyl groups in the PFMPs molecule are bigger in bulk and have more notable steric effects on the polymer chain conformation, hindering the rotation of polymer chains; this makes charge transport and mass diffusion more difficult and slower in solutions and in adsorption layers, and the distances between

the electrochemical active centers of polymers and the electrode surface are increased. This structure effect raises the oxidation potential of the electrode reaction and enlarges ΔE_p , that is, the electrode reaction rate and the reversibility of the PFMPs electrode processes are reduced.

EQCM of two PFS CH_2Cl_2 solutions

The EQCM is a simple, cost effective, high-resolution mass sensing technique, based upon the piezoelectric effect. It can measure the mass change of the electrode surface *in situ* during the electrochemical process, which is effective to understand the mechanism of the electrochemical process.^{18–23} The EQCM of two PFS CH_2Cl_2 solutions were measured *in situ* during CV processes for understanding the mechanism of electrode process. The results are shown in Figure 2.

As shown in Figure 2, during the oxidation scan, the oscillation frequency of quartz changes slightly before the oxidation peak. Then decreases quickly after the oxidation peak reached, it means the mass of the electrode surface increases quickly. During reduction scan, the oscillation frequency of quartz decreases slightly at first, it means that the mass of electrode surface increases slightly. Then oscillation frequency of quartz increases quickly after the reduction peak reached, it means that the mass of electrode surface decreases obviously.

The factors of influence on the mass change of the electrode surface should include adsorption of polymer molecules on the electrode, solvent-swelling of adsorbed polymer layer, and the electrolyte counterions penetrating into the adsorption layer with accompanying solvent molecules. It is quite evident that when the oxidation takes place on the electrode surface in PFS solution, the PFS is oxidized to poly(ferrocenium), polycations, which would separate from CH_2Cl_2 solution and form adsorption layer on the electrode surface due to their low solubility, then the electrolyte anions BF_4^- and solvent molecules would penetrate into the adsorption layer for charge balance. This process would conduce to increase the mass of the electrode surface. By contraries, when the reduction takes place on the electrode surface, the adsorption layer is reduced to neutral state and redissolves into CH_2Cl_2 solution, and the response of EQCM expresses that the mass of the electrode surface decreases. In organic solution, the formed adsorption layer on quartz plate might be a swollen and viscoelastic body. This kind of adsorption layer would be suspicious as nonrigid, and the frequency changes of quartz plate would be less than that predicted by Sauerbrey equation.²⁴ The mass variations associated with solvent and ion exchange between the adsorption layer and the bulk solution would then be underestimated. However, the EQCM responses

of two PFS exhibited that the plot of frequency versus charge showed a linear relationship, which implied that the viscoelastic property of the formed PFS adsorption layer was not dominant, Sauerbrey equation was still valid.^{25–27} So that, the actual mass change of electrode surface (Δm_e) should contain the mass of adsorption layer (Δm_a), the mass of penetrated anions (Δm_i), and the mass of penetrated solvent molecules (Δm_s), that is $\Delta m_e = \Delta m_a + \Delta m_i + \Delta m_s$. In theory, the molar amount of the reacted ferrocene units in electrochemical process can be calculated with the amount of redox charge measured during the CV process, according to the Faraday law ($Q = nFN$, where Q is the amount of reaction charge, which can be obtained from time integral of CV current; n is the electron number of reaction; F is the Faraday constant; N is the molar amount of reac-

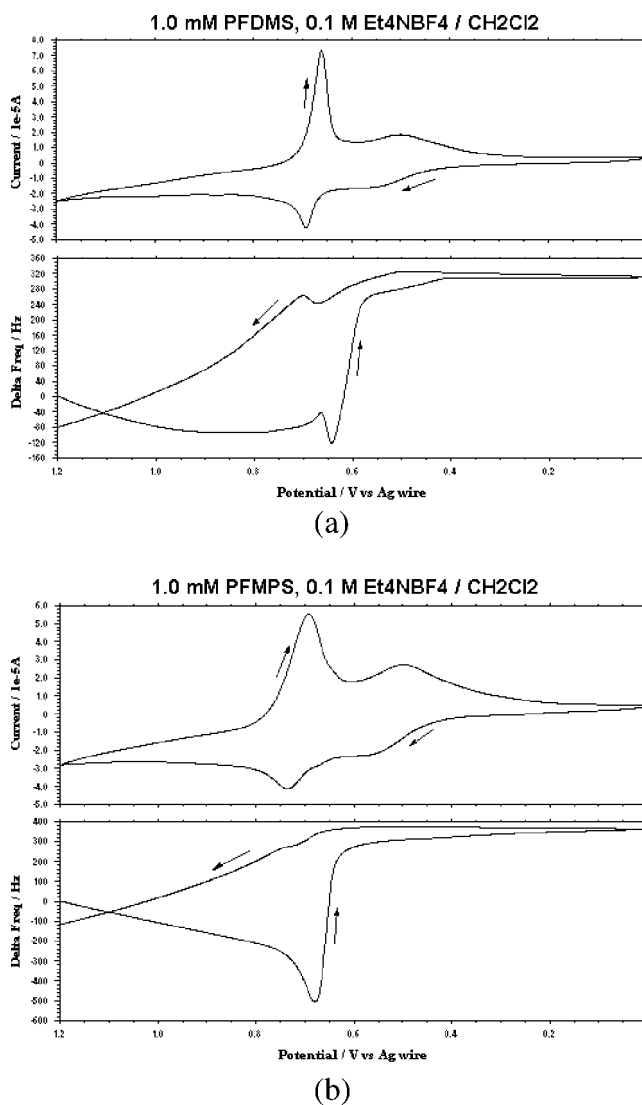


Figure 2 The CV and EQCM spectra of PFS CH_2Cl_2 solutions: (a) PFDMS and (b) PFMPs. PFS concentration: 1.0 mM (in Fe sites), electrolyte concentration: 0.10M Et_4NBF_4 ; scan rates: 60 mV/s; temperature: 25°C. Φ 5 mm Au disk electrode.

TABLE II
The Amount of Reducing Charge Q_c of PFS in CV Process
and the Mass Change Δm_c of the Electrode Surface

PFS	Amount of reducing charge, Q_c (10^{-5}) (C)	Molar amount of reduced polymer, N_c (10^{-10}) (mol)	Δm_a (10^{-7}) (g)	Δm_e (10^{-7}) (g)
PFDMS	7.58	7.86	1.90	4.43
PFMPS	10.2	10.6	3.21	5.15

tant). In redox reaction of ferrocene-based compounds, the electron number of reaction n is equal to one.¹⁵ The amount of reducing charge (Q_c) and the molar amount of reduced polymer (N_c) of two PFS during the CV process at 0.04 V/s scan rate are listed in Table II. The results revealed that the molar amounts of reduced PFS N_c during the CV process were only 7.86×10^{-10} and 10.6×10^{-10} mol, the corresponding mass change of electrode surface, that is the mass of adsorption layer Δm_a ($\Delta m_a = N_c M_{\text{PFS}}$, where M_{PFS} is the molecular weight of PFS) should be 1.90×10^{-7} and 3.21×10^{-7} g, which were much smaller than the actual mass change of the electrode surface Δm_e . It meant that there were counterions and solvent molecules or solvated counterions penetrating into the adsorption layer accompanying with the CV processes for charge balance in the adsorption layer. When the oxidation state of PFS separates from CH_2Cl_2 solution to form an adsorption layer on the electrode surface, the equal molar amount of the electrolyte anions BF_4^- as counterions would penetrate into the adsorption layer for charge neutrality. The molar mass of BF_4^- is 86.8 g/mol, according to one oxidative ferrocene site need one BF_4^- , the calculated mass change of the adsorption layer (ca. 2.58×10^{-7} g for PFDMS, in theory) is still smaller than the actual mass change of the electrode surface Δm_e . It indicated that there are some solvent molecules (ca. three CH_2Cl_2 molecules for PFDMS) penetrating into the adsorption layer.

As shown in Figure 2, the rate of the mass change for oxidation process is slower than that for reduction process, it means that the adsorption layer-forming, counterions and solvent molecules penetrating are slow processes and the dissolution of adsorption layer is quick one. It also means that the counterions and solvent molecules penetrating into the formed adsorption layer play an important role in the electrochemical process.

From Table II, we can see that the reducing charge Q_c of PFMPS is larger than that of PFDMS in CV process, it means that the redox mass N of PFMPS is larger than that of PFDMS. But, we can see from Figure 2, the peak width of PFMPS is broader than that of PFDMS, the peak current of PFMPS is smaller than that of PFDMS, it means that the rate of mass transfer in the PFMPS solution is slower than that in the PFDMS solution.

Kinetics of the electrode process in PFS CH_2Cl_2 solutions

The CV behaviors of two PFS CH_2Cl_2 solutions have indicated that their CV processes are reversible or near-reversible processes. According to the CV theory,²⁸ the CV peak currents i_p (A) rely on the area of work electrode A (cm^2), diffusion coefficient D_0 (cm^2/s), electroactive species concentration C_0^* (mol/cm), and scan rate v (V/s). There is equation for the diffusion-controlled reversible CV process as below:

$$i_p = 0.4463nFA \left(\frac{nF}{RT} \right)^{1/2} D_0^{1/2} C_0^* v^{1/2} \quad (1)$$

The results of linear regression of the CV i_p (the second couple of peaks) and the square root of scan rate $v^{1/2}$ are listed in Table III.

The CV i_p of two PFS are all proportional to the $v^{1/2}$, it demonstrates that the electrode processes in PFS CH_2Cl_2 solutions are all diffusion-controlled. Simultaneously, we notice that the linear relationships of reduction peaks with $v^{1/2}$ are not good as those of oxidation peaks. Because the CV i_p of single layer film is proportional to v and not proportional to $v^{1/2}$, the reduction process of PFS CH_2Cl_2 solution is a complex process in which the diffusion process is dominant and contained the single layer film

TABLE III
The Relationship of CV Currents and Scan Rate of Two PFS CH_2Cl_2 Solutions^a

Polymer solution	Linear equation	Correlation coefficient, r
PFDMS	i_{pa} (μA) = $2.923 - 50.71v^{1/2}$ i_{pc} (μA) = $-0.166 + 87.14v^{1/2}$	-0.9945 0.9899
PFMPS	i_{pa} (μA) = $-0.295 - 25.99v^{1/2}$ i_{pc} (μA) = $-3.754 + 38.767v^{1/2}$	-0.9991 0.9947

^a PFS concentration: 1.0 mM (in Fe sites), electrolyte concentration: 0.10M Et_4NBF_4 ; temperature: 25°C.

TABLE IV
The Diffusion Coefficients D_0 (10^{-6}) (cm^2/s)
of Two PFS in CH_2Cl_2 Solution

Polymer	Anodic peak	Cathodic peak
PFDMS	7.12	21.0
PFMPS	1.87	4.16

process in simultaneity. These phenomena support above-mentioned judgement that the oxidative state of PFS, poly(ferrocenium), forms an adsorption layer on the electrode surface.

The diffusion coefficients D_0 of two PFS CH_2Cl_2 solutions could be calculated with the eq. (1). The results are listed in Table IV.

As shown in Table IV, the D_0 of PFMPS solution is smaller than that of PFDMS solution. This result is consistent with the above discussion. Comparing with the apparent diffusion coefficients D_{app} of PFDMS film and PFMPS film in aqueous solutions, which were obtained in previous studies¹² and were about 1×10^{-11} cm^2/s , we found that the D_0 of PFS in CH_2Cl_2 solution is much larger than those of PFS films in aqueous solutions, it means that the rates of mass transport in PFS CH_2Cl_2 solutions are much quicker than that in the PFS films.

CONCLUSIONS

The studies on the CV of two PFS CH_2Cl_2 solutions indicate that the redox processes of PFS on glassy carbon electrode in CH_2Cl_2 solutions are diffusion-controlled reversible processes. The interaction of active ferrocene centers along the main chain induces the stepwise redox process, and makes the CV waves of the PFS solutions present two couples of peaks. The oxidative state of PFS separate from solution and adsorb on electrode surface to form an adsorption layer during oxidation process, which induce the reduction currents to be larger than the oxidation currents. The molecular structure of polymer has effect on the CV behavior of PFS solution. The large substituent groups on Si bridge restrict the chain motion and decrease the rate of mass transport. So that the peak currents decrease, peak widths increase, peak–peak separations enlarge, and the reversibility of CV processes decrease when the size of the substituent groups on the side chain increased. Calculated diffusion coefficients D_0 of two PFS in

CH_2Cl_2 solution are much larger than those of PFS films in aqueous and organic solutions, it means that the rates of mass transport in PFS CH_2Cl_2 solutions are much quicker than that in the PFS films.

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