

Synthesis of Poly(ferrocenylsilanes) with Different Molecular Weight and Their Electrochemical Behavior

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Received 20 December 2004; accepted 23 July 2005

DOI 10.1002/app.23168

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: A series of poly(ferrocenylsilanes) (PFS) with different molecular weight have been prepared via the thermal ring-opening polymerization of the corresponding monomers. The electrochemical behavior of poly(ferrocenyldimethylsilane) (PFDMS) and poly(ferrocenylmethylphenylsilane) (PFMPS) in solutions were investigated by cyclic voltammetry (CV). It was found that PFS could be adsorbed and electrodeposited on the Pt electrode surface, and the electroactive multilayer films formed on the Pt

electrode surface influenced the shape of the voltammogram. The redox potential varied with the molecular weight slightly, and $\Delta E_{1/2}$ became smaller with the increase in molecular weight. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 473–477, 2006

Key words: poly(ferrocenylsilanes); PFDMS; PFMPS; cyclic voltammetry; peak potential

INTRODUCTION

Researchers have recently paid considerable attention to the investigation and development of new polymer systems that contain transition metals in the main chain because of their useful electronic, electrochemical, and magnetic properties.^{1–5} Ring-opening polymerization of silicon-bridged ferrocenophanes provided access to the first examples of high molecular weight poly(ferrocenylsilanes) (PFS), which are useful materials for modification of electrodes as electrochemical sensors and as nonlinear optical materials.^{6–9} Wang et al.³ and Nguyen et al.¹⁰ have reported the detailed electrochemical studies for films of PFS. In this article, we report the electrochemical behavior of poly(ferrocenyldimethylsilane) (PFDMS) and poly(ferrocenylmethylphenylsilane) (PFMPS) with different molecular weight in solution.

EXPERIMENTAL

Synthesis and characterization of PFS

The PFS were synthesized according to the literature,^{6,11–13} and the structure of the PFS is shown in Scheme 1.

¹H NMR spectra of the resultant polymers were recorded with an advance DMX500 NMR spectrometer in CDCl₃, and tetramethylsilane was used as standards. The ¹H NMR spectrum of PFDMS showed two resonance peaks for the cyclopentadienyl protons at 4.22 and 4.01 ppm and a resonance peak at 0.44 ppm assigned to the methyl groups attached to silicon. The ¹H NMR spectrum of PFMPS showed a resonance peak at 0.64 ppm assigned to the methyl groups attached to silicon and multiple resonance peaks for the cyclopentadienyl protons at 3.87–4.03 ppm and multiple resonance peaks at 7.35–7.56 ppm assigned to the phenyl groups attached to silicon. The molecular weight data of the resultant polymers are shown in Table I.

Solution of PFS

The concentration of PFS was 0.5 mM ferrocenic unit in CH₂Cl₂; 0.1M [Bu₄N][BF₄] was served as a supporting electrolyte.

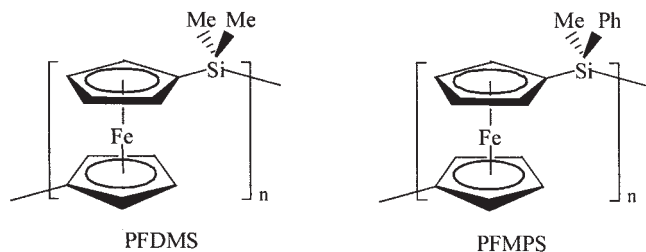
Instruments and reagents

The electrochemical measurements were performed with a CHI-630A electrochemical analyzer (CH Instruments, Inc., Austin, Texas). A one-compartment, three-electrode cell with a Teflon-shrouded Pt plate working electrode ($\varnothing = 2$ mm, geometric area = 0.0314 cm²), a Pt wire counter electrode, and a nonaqueous Ag/Ag⁺ reference electrode was used. All electrodes were purchased from CHI.

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 20174032.

Contract grant sponsor: Ningbo Natural Science Foundation for Doctors.



Scheme 1

The working electrode surface was hand-polished to a mirror finish with $0.05 \mu\text{m}$ Al_2O_3 paste on felt before it was used; then it was washed by an ultrasonic wave with 0.1M NaOH , 1.0M HNO_3 , anhydrous ethyl alcohol, and double-redistilled water in succession. Before the measurements, the solutions were filtered with a $0.45 \mu\text{m}$ microbore filter and purged for at least 10 min with prepurified nitrogen. All the electrochemical measurements were carried out at 25°C . All solvents and analytical- or pure-grade reagents were purchased from commercial sources.

RESULTS AND DISCUSSION

PFDMS and PFMPs were synthesized by the thermal ring-opening polymerization. It has been represented that the molecular weight increased at a range when the thermal ring-opening polymerization time was elongated.¹⁴ The PFS with different molecular weight were attained as shown in Table I. It has been found that there are many factors influencing the electrochemical behavior of PFS.

Influence of different ohmic potential (iR) compensation on cyclic voltammograms

Usually, the solution system showed solution ohmic potential (iR) losses, and obvious difference between the compensated cyclic voltammograms and the uncompensated cyclic voltammograms. So we measured and compensated the iR drop of the investigated 0.1M $[\text{Bu}_4\text{N}][\text{BF}_4]$ solution in CH_2Cl_2 .

The solution iR of PFS with different molecular weight fluctuated from 1550 to 1750 Ω . The typical cyclic voltammograms of PFS are shown in Figure 1. The results indicated that the fluctuation of iR had no obvious influence on the compensated cyclic voltammograms in this investigated solution system.

Influence of the molecular weight on the peak potential

The cyclic voltammetry (CV) behavior of PFDMS and PFMPs with different molecular weight in the same potential scanning rate of 250mV/s was investigated.

The peak potential (E_p) of PFS with the different molecular weight are listed in Table II.

Two-wave cyclic voltammetric behavior of the PFS in solution has been reported and explained by the existence of interactions between the iron centers. It was believed that oxidation of the first ferrocenyl moiety makes the subsequent removal of an electron from a neighboring iron center more difficult.^{15–19}

The experimental results showed that the molecular weight of E_p slightly varied from that of CV. For PFDMS, the peak potentials 1E_p ($^1E_{pa}$ and $^1E_{pc}$), 2E_p ($^2E_{pa}$ and $^2E_{pc}$), and $E_{1/2}$ ($^1E_{1/2}$ and $^2E_{1/2}$) gradually decreased when the molecular weight increased, but for PFMPs, the peak potentials 1E_p and 2E_p increased. The differences in these redox potentials possibly revealed the synergic outcome of the polymeric stereostructure and the electrode adsorption process. To our knowledge, very few studies of relationship between the molecular weight and the redox potential have been previously reported in the literature.^{16,17} The reason is still quite open to discussion.

Manners et al. reported that PFDMS has the glass-transition temperature (T_g) of $\sim 33^\circ\text{C}$ and the T_g of PFMPs is $\sim 90^\circ\text{C}$,^{13,20} which indicates that substituting a phenyl for a methyl in PFDMS decreased the conformational flexibility. On the other hand, the relative steric bulk of phenyl group may result in the fall of density of electroactive sites. Schematic map of PFS oxidation is shown in Figure 2. So the interspace among PFMPs on the surface zone of electrode facilitates the diffusion of supporting electrolyte ions, and PFMPs was oxidized more easily. When the molecular weight of Sample D (PFDMS) was similar to that of Sample a (PFMPs), the redox potentials of PFMPs were smaller than those of PFDMS.

Polymer could be adsorbed and electrodeposited on the Pt electrode surface when PFS in solution was measured as shown in Figure 2. For PFDMS-behaved flexible conformation and symmetrically substituted structure, polymer with the higher molecular weight

TABLE I
Molecular Weight and Molecular Weight Distribution of PFS^a

| Polymer | Sample | M_w (10^4) | M_n (10^4) | PDI |
|---------|--------|------------------|------------------|-----|
| PFDMS | A | 71.1 | 27.9 | 2.5 |
| | B | 32.2 | 14.4 | 2.2 |
| | C | 23.6 | 12.8 | 1.9 |
| | D | 12.2 | 4.0 | 3.0 |
| | E | 5.6 | 2.9 | 1.9 |
| PFMPs | a | 16.0 | 6.6 | 2.4 |
| | b | 2.8 | 1.3 | 2.1 |
| | c | 1.0 | 0.6 | 1.7 |
| | d | 0.5 | 0.1 | 4.7 |

^a Molecular weight were determined by gel permeation chromatography (GPC) in THF containing 0.1% PFS by weight using polystyrene standards.

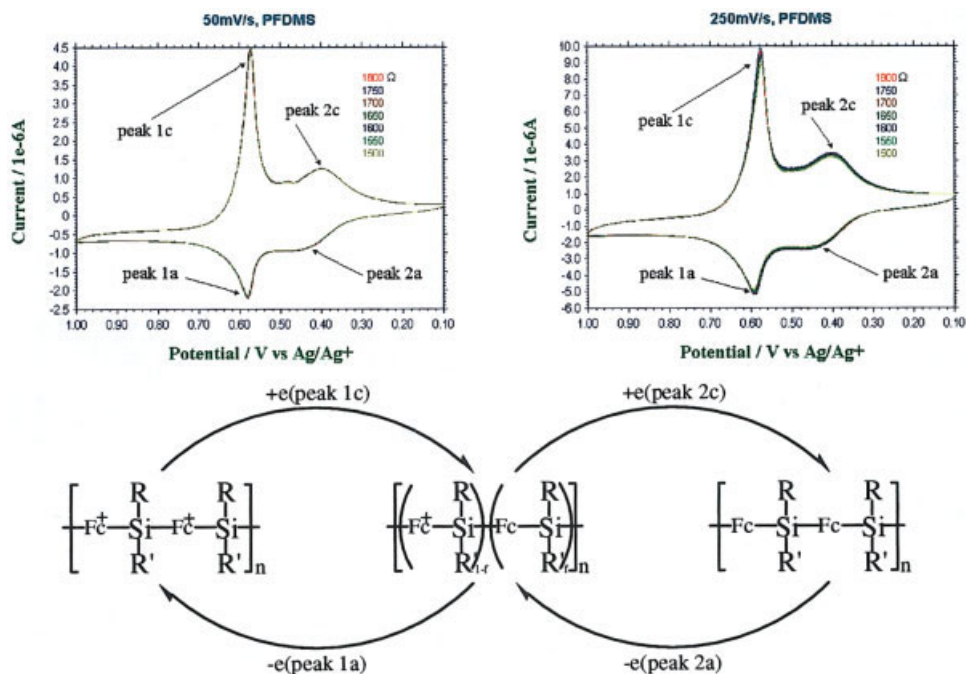


Figure 1 Cyclic voltammogram shape with different iR compensation and corresponding change of polymer (Fc, Ferrocene). PFS samples: containing $0.5 \times 10^{-3} M$ ferrocene unit, $0.1 M$ of $[Bu_4N][BF_4]$ in CH_2Cl_2 at room temperature. Working electrode, Pt plate; counter electrode, Pt wire; reference electrode, a nonaqueous Ag/Ag^+ ; reduction peak, peak 1c and peak 2c; oxidation peak, peak 1a and peak 2a. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

facilitates polymer two-dimension assembly on the Pt electrode surface, though the intensity of electroactive sites (ferrocenyl) is high, they are well assembled,^{21–24} the diffusion of supporting electrolyte ions is easy, and the mixed-value PFS was demonstrated to be a semiconductor.^{25–29} As a result, the peak potentials E_p shifted toward more negative potentials when the molecular weight increased. However, for PFMPs, the relative steric bulk and rigid conformation reduce the intensity of electroactive sites on the electrode surface. When the molecular weight increased, the diffusion of supporting electrolyte ions to the electrode becomes difficult, so the peak potentials E_p shifted positively.

The extent of the interaction between the ferrocenyl units in PFS depends significantly on the nature of the substituents at silicon,^{18,30,31} which may be a result of electronic or conformational effects. The peak separation $\Delta E_{1/2}$ gives a useful measure of the interaction between the iron centers.

It was found that $\Delta E_{1/2}$ increased with the growing chain units when the molecular weight was small.^{16,32} From Table II, we find that ΔE varies from 148 mV (for PFDMS ($M_n = 2.79 \times 10^5$)) to 162 mV (for PFDMS ($M_n = 2.9 \times 10^4$)), and similar phenomena are observed for PFMPs. ΔE decreased when the molecular weight increased. This may be caused by, for example, the

TABLE II
 E_p Data for PFDMS and PFMPs with the Different Molecular Weight from CV

| Polymer | Sample | $^1E_{pc}$ (mV) | $^1E_{pa}$ (mV) | $^1E_{1/2}$ ^a (mV) | $^2E_{pc}$ (mV) | $^2E_{pa}$ (mV) | $^2E_{1/2}$ (mV) | $\Delta E_{1/2}$ ^b (mV) |
|---------|--------|--------------------|--------------------|----------------------------------|--------------------|--------------------|---------------------|---------------------------------------|
| PFDMS | A | 663.5 | 673.8 | 669 | 493.0 | 548.8 | 521 | 148 |
| | B | 665.0 | 676.0 | 671 | 497.0 | | | |
| | C | 679.7 | 692.9 | 686 | 510.6 | 551.8 | 531 | 155 |
| | D | 682.6 | 695.9 | 689 | 506.2 | 556.1 | 531 | 158 |
| | E | 710.6 | 722.3 | 716 | 538.5 | 569.4 | 554 | 162 |
| PFMPs | a | 672.4 | 687.0 | 679.7 | 467.9 | 526.7 | 497.3 | 182 |
| | b | 670.8 | 685.6 | 678.2 | 472.4 | 513.5 | 493.0 | 185 |
| | c | 657.6 | 678.3 | 668.0 | 454.7 | 501.8 | 478.3 | 190 |
| | d | 641.4 | 660.6 | 651.0 | 426.8 | 478.2 | 452.5 | 199 |

^a $^1E_{1/2} = (^1E_{pc} + ^1E_{pa})/2$ and $^2E_{1/2} = (^2E_{pc} + ^2E_{pa})/2$.

^b $\Delta E_{1/2} = ^1E_{1/2} - ^2E_{1/2}$.

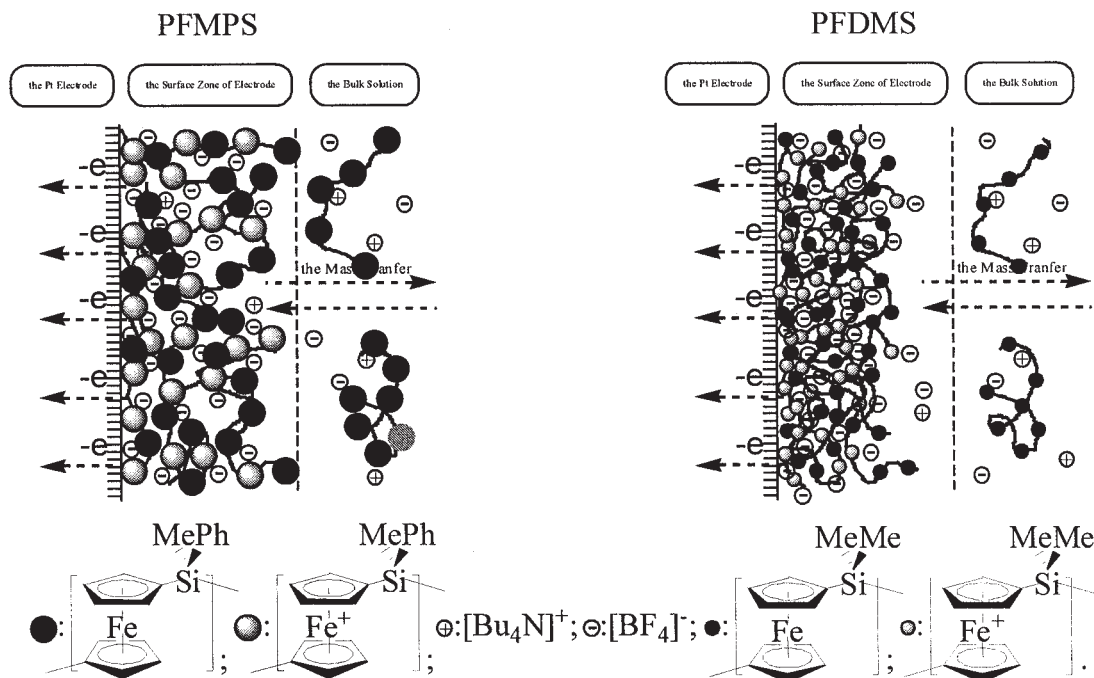


Figure 2 Schematic map of PFS oxidation process.

changes of the better degree of two-dimension assembly on the Pt electrode surface; ordered assembly decreased the interaction between the ferrocenyl units because of increased molecular weight. The results indicate that the extent of the interaction between the ferrocenyl units in PFS also depends on the molecular weight or second-order structure of polymer too. Further research is in progress.

CONCLUSIONS

PFDMS and PFMPS with different molecular weight have been prepared via the thermal ring-opening polymerization. The electrochemical behavior of PFS in CH_2Cl_2 was investigated by CV. Two couples of redox peaks in cyclic voltammograms corresponded to redox processes of PFS, respectively. The fluctuation of iR had no obvious influence on the compensated cyclic voltammograms in measured range. Polymer in solution could be adsorbed and electrodeposited on the Pt electrode surface, and the formed electroactive layer influenced the shape of the voltammogram by affecting the diffusion of the electrolyte ions to the electrode. The peak potentials E_p gradually shifted positively when the molecular weight decreased, but for PFDMS the peak potentials E_p shifted negatively. ΔE increased when the molecular weight decreased.

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