Syntheses and Electrochemical Properties of Siloxane Polymers containing Ferrocene and Dimethylferrocene

T. Inagaki,[a] H. S. Lee,[a] T. A. Skotheim,[a] and Y. Okamoto[b]

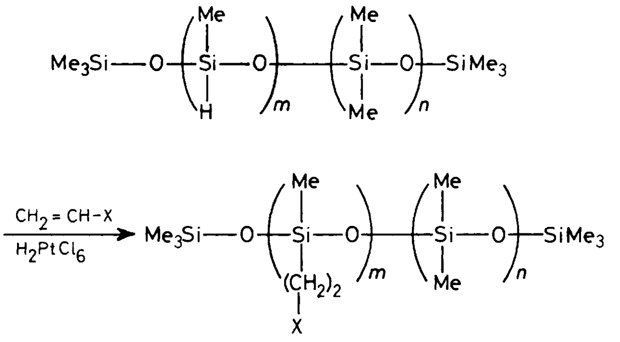
[a] *Materials Science Division, Department of Applied Science, Brookhaven National Laboratory, Upton, NY 11973, U.S.A.*

[b] *Department of Chemistry, Polytechnic University, 333 Jay St., Brooklyn, New York, NY 11201, U.S.A.*

Siloxane polymers containing ferrocene and 1,1′-dimethylferrocene as pendants have been synthesised and characterised; cyclic voltammetry studies using electrodes modified with these polymers showed that the electrochemical properties of ferrocene and 1,1′-dimethylferrocene were maintained.

Recent work in the field of amperometric enzyme electrodes has shown that electron transfer between a redox enzyme and the electrode material can be facilitated by the inclusion of a freely diffusing electroactive mediator, such as TCNQ (tetracyanoquinodimethane)[1] and ferrocene derivatives,[2] in the solution between the electrode surface and its membrane or polymer film coating. In the absence of such mediating species, these electrodes do not respond to variations in the substrate concentration because the distance between the redox centres of the enzyme and the electrode surface is too great to allow efficient electrical communication.

Because these mediators may freely diffuse away from the system, we have designed a network of mediating species covalently bound to a flexible polymer backbone. This polymeric system allows sufficiently close contact between these relays and the enzyme's redox centres so that electrons may be efficiently transferred to the electrode. In this paper, we report the synthesis of siloxane polymers containing ferrocene and 1,1′-dimethylferrocene and discuss the electrochemical behaviour of these polymer films on electrodes. The incorporation of these polymeric mediating networks in amperometric enzyme electrodes is reported elsewhere.[3]



Scheme 1. Preparation of siloxane polymers containing ferrocene and dimethylferrocene. Polymer (**1**): X = ferrocenyl, $m:n = 1:0$. Polymer (**2**): X = ferrocenyl, $m:n = 1:2$. Polymer (**3**): X = 1′,3-dimethylferrocenyl, $m:n = 1:2$.

Methyl(β-ferrocenylethyl)- and methyl-[β-(1′,3′-dimethylferrocenyl)ethyl]siloxane polymers were prepared by the hydrosilylation of vinylferrocene or 1,1′-dimethyl-3-vinylferrocene with methylhydrosiloxane or methylhydrosiloxane–dimethylsiloxane copolymer in the presence of chloroplatinic acid as a catalyst.[4] This synthetic route is described in Scheme 1.

Under nitrogen atmosphere, polymethylhydrosiloxane (Petrarch System, MW 2270) was added into a toluene solution of excess of vinylferrocene in the presence of chloroplatinic acid. After the addition was completed, the reaction mixture was heated to the reflux temperature. The reaction was continued until the Si–H i.r. absorption (2161 cm^{-1})[5] disappeared, showing that all of the starting polymer had been converted to the polymer (**1**). The polymer was purified by repeated reprecipitation from the chloroform solution by dropwise addition into a large excess of acetonitrile at room temperature.

Following the same method as for polymer (**1**), methyl hydrodimethylsiloxane (1:2) copolymer (Petrarch Systems, MW 2000—2100) was treated with vinylferrocene or 1,1′-dimethyl-3-vinylferrocene to give polymers (**2**) or (**3**) as gummy solids.

Cyclic voltammetry (CV) was performed using a Bioanalytical Systems Model CV-27 potentiostat. The electrochemical cell was conventional with a Pt wire working electrode and a Pt-on-glass auxiliary electrode. Potentials were referred to a Ag/AgCl electrode (A-M Systems). Solutions were deaerated by nitrogen bubbling prior to the experiments and the electrochemical cell was kept under nitrogen atmosphere throughout the experiment.

Polymers (**1**), (**2**), and (**3**) were coated on Pt working electrodes by dipping the Pt wire into the chloroform solutions of the polymers. The thickness of the polymer films coated on Pt electrodes could be varied by changing the dipping time and the concentrations of the polymer solutions. The surface coverage, which was calculated from the charge passed by a step-potential method and from cyclic voltammograms, was usually in the range of nmol. equivalents of ferrocene cm^{-2}.

The typical CV data with Et_4NBF_4 in dried MeCN are shown in Figure 1. Reversible redox waves were observed. E^0 values, which are the average of E_{pa} and E_{pc}, were +0.47 V for (**1**) and +0.33 V for (**3**) *vs.* Ag/AgCl. These results were in reasonable agreement with the values obtained from CV of unsubstituted ferrocene (+0.45 V) and 1,1′-dimethylferrocene (+0.32 V) in the same electrolyte and solvent system. The relationships between anodic peak current (i_{pa}) and scan rate (v) calculated from the CV results were $i_{pa} \propto v^{0.8}$ for polymer(**1**) and $i_{pa} \propto v^{0.9}$ for polymer (**3**). The peak separation values (ΔE) were 15 mV for (**1**) and 10 mV for (**3**), at a scan rate of 10 mV s^{-1}.

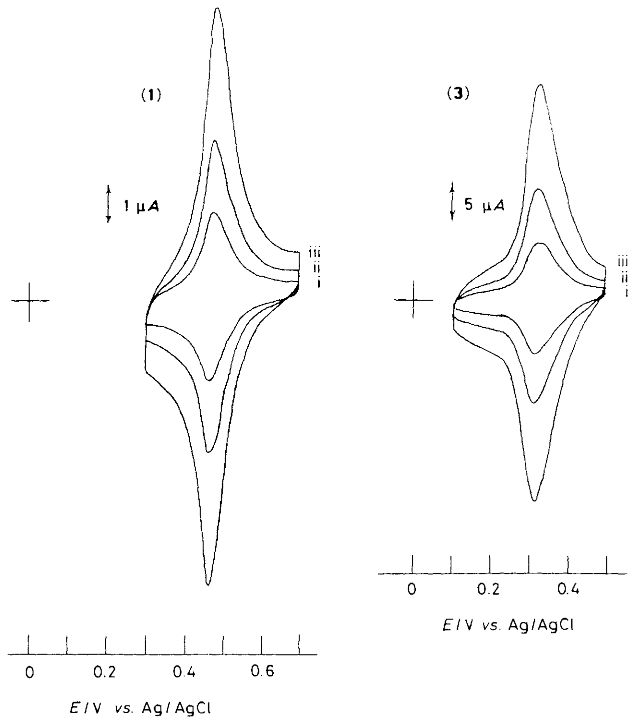


Figure 1. Cyclic voltammograms for polymers (**1**) and (**3**) with 0.2 M Et_4NBF_4/MeCN: (i) 5; (ii) 10; and (iii) 20 mV s^{-1}.

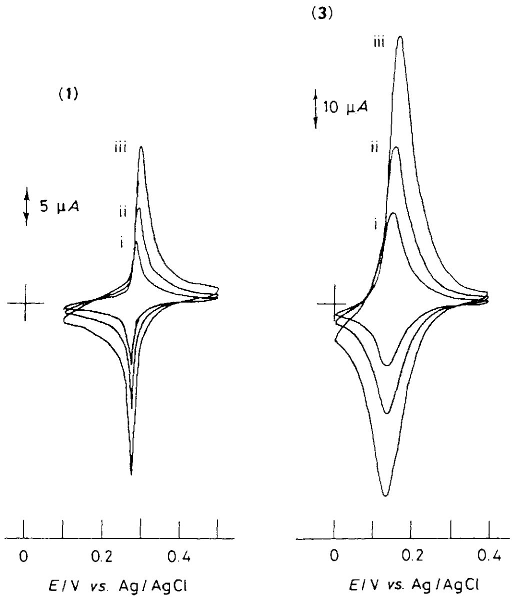


Figure 2. Cyclic voltammograms for polymers (**1**) and (**3**) with 0.2 M Et_4NBF_4/H_2O: (i) 5; (ii) 10; and (iii) 20 mV s^{-1}.

Figure 2 shows CV results in aqueous Et_4NBF_4 solution. E^0 values for each polymer shifted in the cathodic direction owing to the relative change in the potential of Ag/AgCl, which is dependent on the solution conditions. In this solution, the full width at half maximum (E_{FWHM}) values were surprisingly small and decreased as the scan rate decreased. For instance, potential values of 36 mV for the oxidation and 24 mV for the reduction of polymer (**1**) were measured at a scan rate of 10 mV s^{-1}, which were smaller than 90.6/n mV (n = number of electrons transferred per molecule) typically found in the case of surface combined species. This redox behaviour of the ferrocene moieties is most likely related to poor hydrophilicity of the polymer, which affects the diffusion of water and electrolyte into the polymer matrix. These narrow waves have also been reported for polyvinylferrocene.[6] The small E_{FWHM} may indicate attractive or stabilising interactions between redox species.[7]

Cyclic voltammograms obtained in KCl/H_2O gave unstable redox currents which decreased to about 30% of the original electroactivity after 2 h continuous scanning. This decay was observed at various pH values (1.4, 3.7, and 7.2) with KCl and also with KBr as electrolyte. In contrast, very stable redox currents were obtained with Et_4NBF_4/MeCN or Et_4NBF_4/H_2O, which shows that the stability and the electroactivity of these polymer systems are highly dependent on the conditions of the electrochemical experiments.

In summary, we have demonstrated that the preparation of siloxane polymers which contain ferrocene and dimethylferrocene moieties can be accomplished easily and that the electrochemical properties of the ferrocene moieties are maintained in the polymeric system.

The chemical modification of electrodes with such electroactive polymers can lead to many versatile applications, *e.g.*, as biosensors, in electrocatalysis, and in photoelectrochemistry.

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