*Inorg. Chem.* **1995**, *34,* 1668−1680

# Siloxane and Organosilicon Dimers, Monomers, and Polymers with Amide-Linked Ferrocenyl Moieties. Synthesis, Characterization, and Redox Properties

**Carmen M. Casado,[†] Moisés Morán,[†] José Losada,[‡] and Isabel Cuadrado*,[†]**

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad Autónoma de Madrid,
Cantoblanco 28049-Madrid, Spain, and Departamento de Ingeniería Química Industrial, Escuela Técnica
Superior de Ingenieros Industriales, Universidad Politécnica de Madrid, 28006-Madrid, Spain

*Received September 2, 1994*[⊗]

Polymers $[-Si(CH_3)_2(CH_2)_3NHC(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)C(O)NH(CH_2)_3Si(CH_3)_2O-]_n$ (**4**), and $[-C_6H_4C(O)NHCH_2CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)CH_2CH_2NHC(O)C_6H_4Si(CH_3)_2-]_n$ (**5**), in which the amide-linked ferrocenyl moieties are part of the main polymer chain, have been prepared via solution and interfacial polycondensations. As an aid to the spectroscopic and electrochemical characterization, the corresponding dimeric model compounds $[\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4C(O)NH(CH_2)_3Si(CH_3)_2\}]_2\text{-}O$ (**1**), and $[\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4CH_2CH_2NHC(O)(C_6H_4)\}]_2SiMe_2$ (**2**) were synthesized. Electrochemical measurements show that in **1** and **2** the oxidation wave represents a two-electron process, as expected for independent reversible one-electron transfer, at the same potential, of the two ferrocenyl moieties. The cationic dimetallic species $[\mathbf{1}^{2+}][\mathbf{PF_6}^-]_2$ and $[\mathbf{2}^{2+}][\mathbf{PF_6}^-]_2$ have been generated and characterized via infrared spectroelectrochemistry. A redox-active monomer, $\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4C(O)NH(CH_2)_3SiCH_3(OCH_2CH_3)_2\}$ (**3**), has been successfully attached to Pt electrodes and to silica surfaces, via siloxane bond formation. In addition, a series of poly(methylsiloxanes) **6**−**11**, containing pendant ferrocenyl moieties attached to the polymer backbone through amide linkages, with varying degrees of ferrocene substitution, were prepared and characterized. Solution electrochemical studies showed that all the ferrocenyl redox centers present in the polymers are electrochemically independent, and that neutral **6**, **7**, and **10** undergo oxidative precipitation, yielding polymer films on the platinum electrode surfaces. The electrochemistry of electrodes modified with electroactive films of ferrocene-containing polysiloxanes was studied by cyclic voltammetry. Amperometric glucose sensing electrodes based on a ferrocene-containing poly(methylsiloxane) have been prepared.

## Introduction

The synthesis and study of silicon-containing polymers having transition metals in the structure is an area of growing interest since as a result of the incorporation of the metal atoms, such materials exhibit attractive electrical, electrochemical, magnetic, and optical properties.[1−3] In addition, these materials would also be of interest as pyrolytic precursors to transition-metal containing ceramic products.[4]

In our group we are interested in the synthesis of new classes of organometallic species with linear, cyclic,[5] and polyhedral siloxanes, as frameworks for multimetallic compounds and polymers. In this manner, in the last years we have reported the synthesis of some siloxanyl compounds containing $(\eta^6\text{-arene})Cr(CO)_3$ and $[(\eta^5\text{-}C_5R_4)Fe(CO)(\mu\text{-}CO)]_2$ (R = H, Me) moieties.[6] Most recently, a new class of organometallic macromolecules, containing skeletal ferrocenyl and permethylferrocenyl moieties together with silsesquioxane frameworks, has been prepared via hydrosilylation reactions of vinyl substituted ferrocenes with octakis(hydrodimethylsiloxy)octasilsesquioxane.[7]

The objective of the work described here was to extend our studies to new redox-active molecular and macromolecular systems, containing the ferrocenyl moiety together with highly flexible methylsiloxane backbones,[8] and with more rigid organosilicon chains. The ferrocene unit has proved to be a versatile building block with excellent thermal and photochemical stability, which displays a reversible redox reaction in organic solutions. Ferrocenyl-based polymers have been used in the chemical modification of electrodes, in the construction of

---

[†] Universidad Autónoma de Madrid.

[‡] Universidad Politécnica de Madrid.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1995.

(1) (a) *Inorganic and Metal-Containing Polymeric Materials*; Sheats, J. E., Carraher, C. E., Jr., Pittman, C. U., Jr., Zeldin, M., Currell, B., Eds.; Plenum Press: New York, 1990. (b) *Inorganic Polymers*; Mark, J. E., Allcock, H. R., West, R., Eds.; Prentice-Hall, Inc.: Englewood Cliffs, NJ, 1992. (c) *Silicon-Based Polymer Science*; Zeigler, J. M., Gordon Fearon, F. W., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990. (d) *Inorganic and Organometallic Polymers*; Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symposium Series 360; American Chemical Society: Washington, DC, 1988. (e) *Contemporary Polymer Chemistry*, 2nd ed.; Allcock, H. R., Lampe, F. W., Eds.; Prentice Hall: Englewood Cliffs, NJ, 1990. (f) Allcock H. R. *Adv. Mater.* **1994**, *6*, 106.

(2) (a) Foucher, D. A.; Tang, B.; Manners, I. *J. Am. Chem. Soc.* **1992**, *114*, 6246. (b) Manners, I. *J. Inorg. Organomet. Polym.* **1993**, *3*, 185. (c) Manners, I. *Adv. Mater.* **1994**, *6*, 68. (d) Foucher, D. A.; Honeyman, C. H.; Nelson, J. M.; Tang, B. Z.; Manners, I. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1709. (e) Rulkens, R.; Lough, A. J.; Manners, I. *J. Am. Chem. Soc.* **1994**, *116*, 797.

(3) (a) Nguyen, M. T.; Diaz, A. F.; Dement'ev, V. V.; Pannel, K. H. *Chem. Mater.* **1993**, *5*, 1389. (b) Pannel, K. H.; Rozell, J. M., Jr.; Vincenti, S. In *Silicon-Based Polymer Science*; Zeigler, J. M., Gordon Fearon, F. W., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990; p 329.

(4) See, for example: Seyferth, D. In *Silicon-Based Polymer Science*; Zeigler, J. M., Gordon Fearon, F. W., Eds.; Advances in Chemistry Series 224; American Chemical Society: Washington, DC, 1990; p 565.

(5) The synthesis, characterization and electrochemical studies of ferrocenyl-containing tetra- and pentacyclosiloxane molecular compounds and polymers will be reported. Casado, C. M.; Cuadrado, I.; Morán, M.; Losada, J. Manuscript in preparation.

(6) (a) Morán, M.; Cuadrado, I.; Pascual, C.; Losada, J. *Organometallics* **1993**, *12*, 811. (b) Morán, M.; Cuadrado, I.; Pascual, C.; Casado, C. M.; Losada, J. *Organometallics* **1992**, *11*, 1210.

(7) Morán, M.; Casado, C. M.; Cuadrado, I.; Losada, J. *Organometallics* **1993**, *12*, 4327.

(8) Just before this work was submitted for publication, Manners and coworkers reported the synthesis of siloxane-bridged ferrocenophanes. See: Angelakos, C.; Zamble, D. B.; Foucher, D.; Lough, A. J.; Manners, I. *Inorg. Chem.* **1994**, *33*, 1709.

0020-1669/95/1334-1668$09.00/0

amperometric biosensors,[9] and, more recently, in the area of nonlinear optical (NLO) materials.[10]

Specifically, in this paper we report full details on the synthesis, characterization, and redox behavior of a range of poly(methylsiloxanes) and a poly(organosilane), that possess ferrocenyl units attached to the polymer backbone by amide spacer groups, which were prepared by condensation methods. The fact that the ferrocenyl moieties are either a fixed part of the main polymer chain or pendant groups attached to the flexible siloxane backbones is of significance in providing information about the influence of the polymer structure and ferrocene substituent mobility on the physical, chemical and electrochemical properties of these redox-active polymers.

In addition, due to the greater ease of characterization of small molecules compared to macromolecules, the polymers synthesized in this work were characterized by comparison to related model compounds.

## Experimental Section

**General Methods, Materials, and Instrumentation.** All manipulations of air-sensitive materials were carried out under a nitrogen atmosphere using standard Schlenk techniques, and flame-drying glassware when necessary. Solvents were dried over the appropriate drying agents[11] and then distilled and degassed under nitrogen prior to use. Methylhydro(30−35%)dimethylsiloxane(65−70%) copolymer, (aminopropyl)methyl(3−5%)dimethylsiloxane(95−97%) copolymer, (3-aminopropyl)methyldiethoxysilane, 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane, (3-cyanopropyl)methyldichlorosilane, *N*-trimethylsilylallylamine and Karstedt's catalyst (bis(divinyltetramethyldisiloxane)platinum(0), 3−3.5% Pt in xylene) were purchased from Petrarch System and used as received. Triethylamine, $Et_3N$ (Merck), was distilled prior to use. Ferrocenecarboxylic acid, 1,1′-ferrocenedicarboxylic acid and the methiodide of *N,N*-dimethylaminomethylferrocene were purchased from Pluto. Silanized silica gel 60 (70−230 mesh) (Merck) was used for column chromatographic purifications or some filtrations. Dimethylbis(4-chlorocarbonylphenyl)silane was prepared in a three step reaction according to the literature.[12] (Chlorocarbonyl)ferrocene[13] and 1,1′-bis(chlorocarbonyl)ferrocene[14] were prepared as described in the literature. ($\beta$-Aminoethyl)ferrocene and 1,1′-bis($\beta$-aminoethyl)ferrocene were prepared by reduction of ferrocenylacetonitrile and 1,1′-bis(cyanomethyl)ferrocene respectively, with lithium aluminum hydride.[15,16]

Infrared spectra were recorded on a Bomem MB-100 FTIR spectrometer. NMR spectra were recorded on a Bruker-AMX ($^1H$, 300 MHz; $^{13}C$, 75.43 MHz; $^{29}Si$, 59.3 MHz) spectrometer. Chemical shifts are reported in parts per million ($\delta$) with reference to internal tetramethylsilane, $SiMe_4$, or to residual solvent resonances for $^1H$ and $^{13}C$ NMR ($CDCl_3$, $^1H$, $\delta$ 7.27 ppm, $^{13}C$, $\delta$ 77.0 ppm). $^{29}Si$ NMR spectra, referenced externally to tetramethylsilane, were recorded with inverse-gated proton decoupling in order to minimize nuclear Overhauser effects. In some cases the solutions contained 0.015 M $Cr(acac)_3$ in order to reduce $T_1$'s. Solid-state CP/MAS NMR was measured with a Varian Unity 300-MHz spectrometer ($^{13}C$, 75.43 MHz). FAB mass spectral analyses were conducted on a VG Auto Spec mass spectrometer equipped with a cesium ion gun. 3-Nitrobenzyl alcohol was used as the matrix. Number-average molecular weights ($M_n$) were obtained with an Osmomat 070 vapor-pressure osmometer. Elemental analyses were performed by the Microanalytical Laboratory, Universidad Autónoma de Madrid, Madrid, Spain. Thermal analysis of the polymers was effected with a Mettler 181 thermoanalyzer. Samples (10−12 mg) were placed in platinum sample holders. The runs were performed under a nitrogen stream (50 mL/min) and under still air. The samples were heated at a ramp rate of 10 °C/min to a final temperature of 850 °C.

**Electrochemical Measurements.** Cyclic voltammetric experiments were performed on either a PAR 362 potentiostat or a BAS CV-27 potentiostat. Normal pulse voltammetry (NPV) and differential pulse voltammetry (DPV) were carried out with a PAR 174 potentiostat. Coulometric measurements were made with a PAR 362 potentiostat and a PAR 379 digital coulometer. A PAR 377A coulometry cell system fitted with a platinum-gauze working electrode was used.

Electrochemical measurements were performed in acetonitrile, $CH_3CN$ and dichloromethane, $CH_2Cl_2$ (freshly distilled from calcium hydride under nitrogen), tetrahydrofuran, THF (freshly distilled from sodium benzophenone ketyl under nitrogen prior to use), and dimethylformamide, DMF (distilled in vacuo and stored over 4 Å molecular sieves). The supporting electrolyte was in all cases tetra-*n*-butylammonium hexafluorophosphate (TBAH) which was purchased from BAS or Strem and was purified by recrystallization from ethanol and dried in vacuo at 60 °C. The supporting electrolyte concentration was typically 0.1 M. All cyclic voltammetric experiments were performed using either a platinum-disk working electrode ($A = 0.070$ cm$^2$) or a glassy carbon-disk working electrode ($A = 0.070$ cm$^2$) each of which was polished prior to use with 1-$\mu$m diamond paste (Buehler) and rinsed thoroughly with water and acetone. All potentials are referenced to the saturated calomel electrode (SCE). A coiled platinum wire was used as a counterelectrode and the electrochemical cells were of conventional design. Solutions for cyclic voltammetry were typically 1.0 mM in the redox active species and were deoxygenated by purging with prepurified nitrogen. No *iR* compensation was used. NPV measurements were performed using a platinum-disk working electrode ($A = 0.008$ cm$^2$) sealed in glass, at a scan rate of 10 mV/s.

**Modification of Electrodes.** For chemical modification of platinum-disk electrodes via silanization, the electrodes were anodized to form an oxide layer on the surface by holding the potential at +1.9 V in 0.5 M sulfuric acid, followed by cycling between +1.23 and −0.25 V (100 mV/s) until the cyclic voltammograms were constant. The potential was then held at +1.1 V until the current decayed to small values (<1 $\mu$A/cm$^2$). The anodized electrode was removed from the cell, washed thoroughly with distilled water and methanol, and vacuum oven dried (20−45 min, 50 °C). The electrodes were placed in Schlenk tubes maintained under nitrogen and containing the ethoxysilyl compound **3** in toluene solution. The reaction temperature was maintained between 25 and 70 °C and the reaction time varied from 2 to 6 h. The electrodes were then removed from solution, rinsed several times with dry dichloromethane, dried, and stored under vacuo.

For modification of glassy-carbon-disk electrodes with films of **3** immobilized on silica, a suspension containing approximately 0.1 g of the derivatized silica and 0.01 g of polystyrene per milliliter of dichloromethane was prepared. Several drops of this suspension were placed on a freshly polished glassy carbon electrode ($A = 0.070$ cm$^2$) and allowed to evaporate to dryness.

The preparation of electrodes coated with evaporatively deposited polymer films was accomplished by micropipetting a few microliters of tetrahydrofuran or dichloromethane solutions containing about 1 mg/mL of polymer onto the platinum or glassy-carbon-disk electrode surface and allowing the solvent to evaporate to dryness.

The polymer/glucose oxidase/carbon paste electrode was constructed by mixing 0.54 mg of polymer **10**, previously dissolved in dichlo-

---

(9) See for example: (a) Hendry, S. P.; Cardosi, M. F.; Turner, A. P. F. *Anal. Chim. Acta* **1993**, *281*, 453. (b) Hale, P. D.; Lan, H. L.; Boguslavsky, L. I.; Karan, H. I.; Okamoto, Y.; Skotheim, T. A. *Anal. Chim. Acta* **1991**, *251*, 121. (c) Hale, P. D.; Boguslavsky, L. I.; Inagaki, T.; Karan, H. I.; Lee, H. S.; Skotheim, T. A.; Okamoto, Y. *Anal. Chem.* **1991**, *63*, 677. (d) Hale, P. D.; Inagaki, T.; Karan, H. I.; Okamoto, Y.; Skotheim, T. A. *J. Am. Chem. Soc.* **1989**, *111*, 3482. (e) Inagaki, T.; Lee, H. S.; Skotheim, T. A.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1181. (f) Hale, P. D.; Inagaki, T.; Lee, H. S.; Karan, H. I.; Okamoto, Y.; Skotheim, T. A. *Anal. Chim. Acta* **1990**, *228*, 31.

(10) For recent works on ferrocenyl-containing NLO materials see, for example: (a) Wright, M. E.; Toplikar, E. G. *Macromolecules* **1992**, *25*, 6050. (b) Wright, M. E.; Sigman, M. S. *Macromolecules* **1992**, *25*, 6055. (c) Togni, A.; Rihs, G. *Organometallics* **1993**, *12*, 3368.

(11) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: New York, 1988.

(12) Ghatge, N. D.; Jadhav, J. Y. *Synth. React. Inorg. Met.-Org. Chem.* **1984**, *14*, 83.

(13) Pauson, P. L.; Watts, W. E. *J. Chem. Soc.* **1963**, 2990.

(14) Knobloch, F. W.; Rauscher, W. H. *J. Polym. Sci.* **1961**, *54*, 651.

(15) Gonsalves, K. E.; Lenz, R. W.; Rausch, M. D. *Appl. Organomet. Chem.* **1987**, *1*, 81.

(16) (a) Pittman, C. U., Jr.; Voges, R. L.; Jones, W. *Macromolecules* **1971**, *4*, 296. (b) Ratajczak, A.; Czech, B.; Drobek, L. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 557.

romethane, with 50 mg of graphite powder. After evaporation of the solvent, 5 mg of glucose oxidase and 10 $\mu$L of paraffin oil were added, and the mixture was blended into a paste. The paste was placed in a carbon paste electrode (BAS MF-2010) ($A = 0.07$ cm$^2$). All solutions, even glucose samples injected, were deoxygenated by bubbling $N_2$. In the constant potential experiments, a gentle flow of $N_2$ was also used to facilitate stirring; the background current was allowed to reach a constant value before samples of glucose were added.

**Spectroelectrochemical Experiments.** Infrared spectral changes during thin-layer bulk electrolyses were measured by using a spectroelectrochemical cell as described previously.[6b] Infrared data were collected with a Bomem MB-100 FTIR spectrometer. Bulk electrolyses were controlled by a PAR 362 potentiostat.

**Synthesis of Model Compound $[\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4C(O)NH(CH_2)_3Si(CH_3)_2\}]_2\text{–}O$ (1).** 1,3-Bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (0.8 g, 3.22 mmol) and triethylamine (1.30 g, 12.88 mmol) were dissolved in dry toluene (50 mL) in a three-necked, 250 mL flask fitted with a reflux condenser, a dropping funnel, $N_2$ inlet, and magnetic stir bar. (Chlorocarbonyl)ferrocene (1.6 g, 6.44 mmol) in dry toluene (40 mL) was added dropwise into the stirred solution, and an immediate yellow precipitate resulted while a slight increase of the temperature was observed. Stirring was continued for 15 min, and the solid was filtered and purified chromatographically (2 × 30 cm) on silanized silica using a dichloromethane/acetone (10:1 v/v) mixture as eluent. The yellow band was collected and solvent removal afforded a yellow-orange solid. Yield: 1.90 g, 88%. Recrystallization by slow diffusion of hexane in a concentrated solution of the solid in dichloromethane gave **1** as orange needles. $^1$H NMR ($CDCl_3$): $\delta$ 6.31 (t, 1H, N*H*), 4.75 (t, 2H, $C_5H_4$), 4.33 (t, 2H, $C_5H_4$), 4.21 (s, 5H, Cp), 3.35 (m, 2H, $NHCH_2$), 1.63 (m, 2H, $CH_2CH_2CH_2$), 0.57 (m, 2H, $CH_2Si$), 0.07 (s, 3H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 170.07 (*C*O), 76.34 (OC–$C_5H_4$), 70.11 ($C_5H_4$), 69.56 (Cp), 68.13 ($C_5H_4$), 42.44 (NH–$CH_2$), 23.85 ($CH_2CH_2CH_2$), 15.48 (Si–$CH_2$), 0.26 (Si–$CH_3$). MS (FAB; *m/z* (%)): 672 ($M^+$, 100), 607 ($M^+ - C_5H_5$, 21.60), 402 ($M^+ - [(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4C(O)NH(CH_2)_3]$, 5.47), 328 ($[\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4C(O)NH(CH_2)_3Si(CH_3)_2\}]^+$, 46.57), 213 ($[\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4C(O)\}]^+$, 36.60), 185 ($[\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4\}]^+$, 14.92), 121 ($[\{\eta^5\text{-}C_5H_5\}Fe]^+$, 7.79). IR (KBr): amide I, 1626 cm$^{-1}$; amide II, 1546 cm$^{-1}$; amide III, 1306 cm$^{-1}$. Anal. Calcd for $C_{32}H_{44}N_2Fe_2Si_2O_3$: C, 57.15; H, 6.59; N, 4.17. Found: C, 57.21; H, 6.63; N, 4.09.

**Synthesis of Model Compound $[\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4CH_2CH_2NHC(O)(C_6H_4)\}]_2\text{–}SiMe_2$ (2).** In a 250-mL round-bottom flask, fitted with a dropping funnel, $N_2$ inlet, and magnetic stir bar, were placed 30 mL of dry dichloromethane, ($\beta$-aminoethyl)ferrocene (1 g, 4.37 mmol), and triethylamine (0.88 g, 8.74 mmol). To this solution was added dropwise dimethylbis(4-chlorocarbonylphenyl)silane (0.73 g, 2.18 mmol) also in 30 mL of dry dichloromethane. After 15 min of stirring at room temperature, the reaction completion was confirmed by FTIR spectroscopy, which showed the absence of the bands at 1774 and 1731 cm$^{-1}$ due to the starting dichlorocarbonylsilane and the appearance of two new absorbances at 1661 and 1522 cm$^{-1}$ corresponding to the new amide group in the dimer. After evaporation of the solvent under vacuo, the resulting residue was purified by treatment with benzene to remove the insoluble triethylamine hydrochloride subproduct and further recrystallization from dichloromethane solution into acetonitrile to yield a yellow orange solid (1.33 g, 85%). This compound was also synthesized by aqueous interfacial condensation, following a procedure similar to that described bellow in method B for polymer **5**. $^1$H NMR ($CD_3COCD_3$): $\delta$ 7.87 (d, 2H, $C_6H_4$), 7.63 (d, 2H, $C_6H_4$), 7.82 (t, 1H, N*H*), 4.14 (s, 5H, Cp), 4.13 (t, 2H, $C_5H_4$), 4.05 (t, 2H, $C_5H_4$), 3.57 (m, 2H, $NHCH_2$), 2.64 (t, 2H, $CH_2C_5H_4$), 0.61 (s, 3H, $SiCH_3$). $^1$H NMR ($CDCl_3$), broad signals, but useful for comparative purposes: $\delta$ 7.68 (br, 2H, $C_6H_4$), 7.55 (br, 2H, $C_6H_4$), 6.20 (br, 1H, N*H*), 4.12 (br, 9H, $C_5H_4$, $C_5H_5$), 3.58 (br, 2H, $NHCH_2$), 2.66 (br, 2H, $CH_2C_5H_4$), 0.57 (s, 3H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 167.18 (*C*O), 141.79 (OC–$C_6H_4$), 135.34 (Si–$C_6H_4$), 134.30 (*m*-$C_6H_4$Si), 126.02 (*o*-$C_6H_4$Si), 85.29 ($CH_2$–$C_5H_4$), 68.61 (Cp), 68.25, 67.69 ($C_5H_4$), 41.11 (NH–$CH_2$), 29.67 ($CH_2$–$C_5H_4$), −2.71 (Si–$CH_3$). MS (FAB; *m/z* (%)): 722 ($M^+$, 100), 657 ($M^+ - C_5H_5$, 33.98), 537 ($M^+ - [(\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)]$, 6.06), 212 ($[\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4CH_2CH_2\}]^+$, 48.77), 199 ($[\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4CH_2\}]^+$, 24.71), 121 ($[\{\eta^5\text{-}C_5H_5\}Fe]^+$, 13.31). IR (KBr): amide I, 1638 cm$^{-1}$; amide II, 1539 cm$^{-1}$; amide III, 1309 cm$^{-1}$. Anal. Calcd for $C_{40}H_{42}N_2O_2SiFe_2$: C, 66.49; H, 5.86; N, 3.88. Found: C, 66.40; H, 5.79; N, 3.91.

**Synthesis of $\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4C(O)NH(CH_2)_3SiCH_3(OCH_2CH_3)_2\}$ (3).** Compound **3** was prepared similarly to model **1** starting from (chlorocarbonyl)ferrocene (1.50 g, 6.02 mmol), (3-aminopropyl)-methyldiethoxysilane (1.15 g, 6.01 mmol), and triethylamine (1.22 g, 12.06 mmol). In this case the monomer is soluble in toluene, and only the triethylamine hydrochloride subproduct precipitates, which is removed by filtration through a short column of silanized silica. The filtrate is evaporated to dryness, and the residue is purified by recrystallization in acetonitrile yielding 81% of monomer **3** as a yellow-orange solid. This product can be also isolated as orange needles by slow diffusion of hexane in a concentrated solution of the solid in dichloromethane. $^1$H NMR ($CDCl_3$): $\delta$ 5.89 (t, 1H, N*H*), 4.66 (t, 2H, $C_5H_4$), 4.33 (t, 2H, $C_5H_4$), 4.20 (s, 5H, Cp), 3.79 (m, 2H, $OCH_2CH_3$), 3.38 (m, 2H, $NHCH_2$), 1.68 (m, 2H, $CH_2CH_2CH_2$), 1.23 (t, 3H, $OCH_2CH_3$), 0.68 (m, 2H, $CH_2Si$), 0.15 (s, 3H, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 169.95 (*C*O), 76.39 (OC–$C_5H_4$), 70.10 ($C_5H_4$), 69.55 (Cp), 67.96 ($C_5H_4$), 58.03 ($OCH_2CH_3$), 41.88 (NH–$CH_2$), 18.29 ($OCH_2CH_3$), 23.20 ($CH_2CH_2CH_2$), 11.18 (Si–$CH_2$), 3.80 (Si–$CH_3$). IR (KBr): amide I, 1626 cm$^{-1}$; amide II, 1541 cm$^{-1}$; amide III, 1306 cm$^{-1}$. Anal. Calcd for $C_{19}H_{29}NO_3SiFe$: C, 56.57; H, 7.25; N, 3.47. Found: C, 56.48; H, 7.19; N, 3.55.

**Immobilization of 3 on Silica Surfaces.** To immobilize compound **3** onto silica surfaces, the $SiO_2$ gel 100 (Merck, 0.063–0.200 mm, 70–230 mesh) was previously treated with dry methanol under reflux and dried under vacuo at 150 °C for 15 h. The silica (ca. 1 g) was then reacted with **3** (3 mmol) in toluene (30 mL) at 85–90 °C for 24 h. The resulting silica material was isolated by filtration, and washed several times with toluene and subsequently with dichloromethane, with the last two washings being colorless. The light-orange powder was dried under vacuum at 40 °C. Anal. Found: C, 11.73; N, 1.02; Fe, 4.09. The analysis is consistent with a coverage of ferrocenyl units of 7.32 × 10$^{-4}$ mol/g. IR (KBr): amide I, 1634 cm$^{-1}$; amide II, 1541 cm$^{-1}$.

**Polymer Syntheses.** Two condensation methods were used for the preparation of the polymers **4–11**. Representative preparations of several polymers are described here. Other syntheses were analogous.

**Method A. Solution Condensation. Synthesis of Polymer 4.** A solution of 1,1′-bis(chlorocarbonyl)ferrocene (1.53 g, 4.92 mmol) in toluene (20 mL) was added quickly, under stirring, to a chilled (0 °C) toluene solution (20 mL) of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane (1.22 g, 4.92 mmol) and triethylamine (1.98 g, 19.68 mmol). After 15 min the resulting yellow solid was collected by filtration and treated with acetonitrile overnight. The insoluble residue was further treated with dichloromethane and a highly insoluble dark orange solid was separated, which could be characterized only by IR spectroscopy. The dichloromethane solution was then concentrated and added dropwise to a large excess of acetonitrile, affording a yellow-orange solid, which was washed with acetonitrile and dried in vacuo. Yield: 1.24 g (52%). $M_n$ (VPO, $CH_2Cl_2$): 10 600. $^1$H NMR ($CDCl_3$): $\delta$ 6.59 (br t, N*H*), 4.52 (br t, $C_5H_4$), 4.38 (br t, $C_5H_4$), 3.37 (m, $NHCH_2$), 1.73 (m, $CH_2CH_2CH_2$), 0.60 (m, $CH_2Si$), 0.09 (s, $SiCH_3$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta$ 70.51 ($C_5H_4$), 42.65 (NH–$CH_2$), 23.85 ($CH_2CH_2CH_2$), 15.70 (Si–$CH_2$), 0.48 (Si–$CH_3$). $^{29}Si\{^1H\}$ NMR ($CDCl_3$): $\delta$ 7.63. IR (KBr): amide I, 1634 cm$^{-1}$; amide II, 1548 cm$^{-1}$; amide III, 1299 cm$^{-1}$. Anal. Calcd for $[C_{22}H_{34}N_2O_3Si_2Fe]_n$: C, 54.30; H, 6.99; N, 5.76. Found: C, 53.90; H, 6.91; N, 5.67. Polymer **4** was also synthesized by method B.

**Method B. Interfacial Condensation. Synthesis of Polymer 5.** In a 100 mL round-bottom flask equipped with a Ultra-Turrax T25 (Janke & Kunkel) blender and a wide-mouth addition funnel, a mixture of 1,1′-bis($\beta$-aminoethyl)ferrocene (0.15 g, 0.55 mmol) and triethylamine (0.34 g, 3.37 mmol) in deoxygenated water (30 mL) were stirred at 8000 rpm. A solution of dimethylbis(4-chlorocarbonylphenyl)silane (0.25 g, 0.74 mmol) in $CCl_4$ (30 mL) was added in one fell swoop and the stirring speed was turned to 24 000 rpm for 5 min. A yellow-orange emulsion with some gummy product was formed, and after decantation, it was worked up with acetonitrile. The residue insoluble in $CH_3CN$ was dissolved in $CH_2Cl_2$ and subsequently purified by reprecipitation from dichloromethane/acetonitrile to yield polymer **5** as a yellow solid. Yield: 0.14 g (48%). An orange insoluble solid was primarily isolated from the dichloromethane solution, but its high insolubility prevented its accurate characterization. $M_n$ (VPO, $\mathrm{CH_2Cl_2}$): 12 500. $^1$H NMR ($\mathrm{CDCl_3}$): $\delta$ 7.76 (d, $\mathrm{C_6}H_4$), 7.53 (d, $\mathrm{C_6}H_4$), 6.71 (br, N$H$), 4.08 (br, $\mathrm{C_5}H_4$), 3.99 (br, $\mathrm{C_5}H_4$), 3.56 (br m, NHC$H_2$), 2.65 (br m, $CH_2\mathrm{C_5H_4}$), 0.59 (s, SiC$H_3$). $^{13}$C{$^1$H} NMR ($\mathrm{CDCl_3}$): $\delta$ 168.22 ($C$O), 142.00 (OC$-C_6\mathrm{H_4}$), 135.68 (Si$-C_6\mathrm{H_4}$), 134.33 ($m$-$C_6\mathrm{H_4}$-Si), 125.15 ($o$-$C_6\mathrm{H_4}$Si), 83.63 (OC$-C_5\mathrm{H_4}$), 67.80, 67.70 ($C_5\mathrm{H_4}$), 41.23 (NH$-C\mathrm{H_2}$), 29.65 ($C\mathrm{H_2}-\mathrm{C_5H_4}$), $-2.70$ (Si$-C\mathrm{H_3}$). $^{29}$Si{$^1$H} NMR ($\mathrm{CDCl_3}$): $\delta$ $-7.39$. IR (KBr): amide I, 1641 cm$^{-1}$; amide II, 1534 cm$^{-1}$; amide III, 1303 cm$^{-1}$. Anal. Calcd for $[\mathrm{C_{30}H_{32}N_2O_2SiFe}]_n$: C, 67.16; H, 6.01; N, 5.22. Found: C, 65.97; H, 5.87; N, 5.11.

**Synthesis of Polymer 6.** The preparation of the polysiloxane (aminopropyl)methyl(30−35%)dimethylsiloxane(65−70%) copolymer was adapted from a literature procedure for the preparation of poly(dimethylsiloxanes) containing $\gamma$-aminopropyl groups.[17] Methylhydro(30−35%)dimethylsiloxane(65−70%) copolymer (5 g, ≈23.35 mmol SiH), $N$-trimethylsilylallylamine (30.2 g, 233.5 mmol), and Karstedt's catalyst (100 $\mu$L of a 3−3.5% solution in xylene) in 150 mL of dry toluene were heated under reflux for 18 h. IR showed complete reaction of the Si−H groups. Ethanol (85 mL) was added and the mixture was refluxed for 1 h, to remove the trimethylsilyl groups. Solvents and volatiles were removed in vacuo and the residue was taken up in petroleum ether, washed with salt water, dried, and evaporated to dryness. The polymer was kept in petroleum ether solution to prevent cross-linking.

A portion of this polysiloxane thus obtained (1.64 g, ≈6.03 mmol of $\mathrm{NH_2}$) was reacted with (chlorocarbonyl)ferrocene (1.75 g, 7.03 mmol) in toluene and in the presence of triethylamine, as described above in method A. Polymer **6** was isolated as a thick product that hardens and solidifies on standing, resulting in an orange shiny material (1.9 g). $M_n$ (VPO, $\mathrm{CH_2Cl_2}$): 4800. $^1$H NMR ($\mathrm{CDCl_3}$): $\delta$ 5.85 (br, N$H$), 4.60 (br, $\mathrm{C_5}H_4$), 4.34 (br, $\mathrm{C_5}H_4$), 4,20 (br, Cp), 3.37 (m, NHC$H_2$), 1.65 (m, $\mathrm{CH_2}CH_2\mathrm{CH_2}$), 0.60 (m, $CH_2$Si), 0.07 (s, SiC$H_3$). IR (KBr): amide I, 1632 cm$^{-1}$; amide II, 1548 cm$^{-1}$. Anal. Calcd for $x = 0.34$, $y = 0.66$: C, 49.54; H, 6.90; N, 2.98. Found: C, 49.11; H, 6.73; N, 2.88.

**Synthesis of Polymer 7.** Polymer **7** was prepared following method A, starting from (chlorocarbonyl)ferrocene (2 g, 8.05 mmol) and (aminopropyl)methyl(3−5%)dimethylsiloxane(95−97%) copolymer (19 g, ≈7.41 mmol of $\mathrm{NH_2}$) in a benzene solution in the presence of triethylamine. It was isolated as an orange viscous oil (14.6 g). $M_n$ (VPO, $\mathrm{CH_2Cl_2}$): 8850. $^1$H NMR ($\mathrm{CDCl_3}$): $\delta$ 5.72 (t, N$H$), 4.64 (t, $\mathrm{C_5}H_4$), 4.32 (t, $\mathrm{C_5}H_4$), 4.19 (s, Cp), 3.35 (m, NHC$H_2$), 1.63 (m, $\mathrm{CH_2}CH_2\mathrm{CH_2}$), 0.57 (m, $CH_2$Si), 0.07 (s, SiC$H_3$). $^{13}$C{$^1$H} NMR ($\mathrm{CDCl_3}$): 70.22 ($C_5\mathrm{H_4}$), 69.72 (Cp), 68.02 ($C_5\mathrm{H_4}$), 42.22 (NH$-C\mathrm{H_2}$), 23.63 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$), 14.70 (Si$-C\mathrm{H_2}$), 1.80, 1.04 (Si$-C\mathrm{H_3}$). $^{29}$Si{$^1$H} NMR ($\mathrm{CDCl_3}$): $\delta$ 7.08, $-19.06$, $-22.08$. IR (KBr): amide I, 1631 cm$^{-1}$; amide II, 1545 cm$^{-1}$. Anal. Calcd for $x = 0.03$, $y = 0.97$: C, 35.27; H, 7.94; N, 0.50. Found: C, 34.15; H, 8.05; N, 0.60.

**Synthesis of Polymer 8.** Following method A, 1,1′-bis(chlorocarbonyl)ferrocene (2.00 g, 6.43 mmol) in toluene was added dropwise to a chilled stirred solution of (aminopropyl)methyl(30−35%)dimethylsiloxane(65−70%) copolymer (2.90 g, ≈10.65 mmol of $\mathrm{NH_2}$) and triethylamine (2.6 g, 25.7 mmol). A red gelatinous product was formed. Toluene was removed under vacuo, and the residue was treated with dichloromethane overnight and subsequently with acetone. The insoluble material was then filtrated and dried under vacuum, resulting a shiny dark orange solid. However, the insolubility of this polymer prevented its complete purification and characterization. IR (KBr): amide I, 1636 cm$^{-1}$; amide II, 1541 cm$^{-1}$.

**Synthesis of Polymer 9.** Polymer **9** was synthesized by method B, adding a solution of 1,1′-bis(chlorocarbonyl)ferrocene (0.35 g, 1.12 mmol) in acetonitrile (25 mL) to a vigorously stirred solution of (aminopropyl)methyl(3−5%)dimethylsiloxane(95−97%) copolymer (4.10 g, ≈1.6 mmol of $\mathrm{NH_2}$) and triethylamine (0.5 g, 4.8 mmol) in hexane (25 mL). A total of 2.5 g of the desired polymer was isolated as a dark orange waxy material. $^1$H NMR ($\mathrm{CDCl_3}$): $\delta$ 6.75 (br, N$H$), 4.48 (br, $\mathrm{C_5}H_4$), 4.43 (br, $\mathrm{C_5}H_4$), 3.38 (br, NHC$H_2$), 1.67 (br, $\mathrm{CH_2}CH_2\mathrm{CH_2}$), 0.59 (br, $CH_2$Si), 0.07 (s, SiC$H_3$). IR (KBr): amide I, 1632 cm$^{-1}$; amide II, 1549 cm$^{-1}$. Anal. Calcd for $x = 0.03$, $y = 0.97$: C, 34.26; H, 8.02; N, 0.52. Found: C, 33.87; H, 7.93; N, 0.56.

**Synthesis of Poly[(3-chlorocarbonylpropyl)methylsiloxane].** This prepolymer was prepared by a modification of literature procedures.[18] To 80 mL of chilled water (0−5 °C) was slowly added a solution of (3-cyanopropyl)methyldichlorosilane (45.49 g, 0.25 mol) in diethyl ether (80 mL). The product was extracted with diethyl ether and the solvent was removed by rotary evaporation. An aliquot (20 mL) of the residue was treated with sulfuric acid 50% (40 mL) at 90 °C for 24 h under stirring. While that temperature was maintained, the aqueous layer was separated and poured into 2 L of cold water to obtain a white precipitate. This product was thoroughly rinsed with water and heated to 90 °C in vacuo for 8 h to afford poly[(3-carboxypropyl)methylsiloxane] as a rubber-like white product. IR: $\nu$(CO), 1709 cm$^{-1}$. $M_n$: 4500. To a solution of poly[(3-carboxypropyl)methylsiloxane] (3.16 g, ≈0.7 mmol) in dry chloroform (60 mL) and under dinitrogen, 80 mL of thionyl chloride were added. The mixture was stirred at room temperature overnight. The solvent and excess of thionyl chloride were removed under vacuo and poly[(3-chlorocarbonylpropyl)methylsiloxane] was obtained as a dense whitish product (IR $\nu$(CO) 1796 cm$^{-1}$). Due to the high sensitivity of this polysiloxane to the moisture, further manipulations were carried out under an inert atmosphere and storage for long periods of time was avoided.

**Synthesis of Polymer 10.** As described in method A, a solution of poly[(3-chlorocarbonyl)propylmethylsiloxane (0.70 g, ≈4.2 mmol of COCl) in dichloromethane was added dropwise to another solution of ($\beta$-aminoethyl)ferrocene (1.5 g, 6.55 mmol) and triethylamine (1.33 g, 13.11 mmol) in the same solvent. The reaction was completed in 30 min, as was indicated by IR spectroscopy by monitoring the loss of the $\nu$(CO) absorption at 1790 cm$^{-1}$ and the appearance of two new bands at 1643 and 1548 cm$^{-1}$ due to the condensation product. After removal of the solvent under vacuum, the residue was treated with toluene, and the triethylamine hydrochloride byproduct was separated. Successive reprecipitations from dichloromethane into acetonitrile afforded polymer **10** as a bright brown solid. Yield: 0.98 g, ≈70%. $M_n$ (VPO, $\mathrm{CH_2Cl_2}$): 10 800. $^1$H NMR ($\mathrm{CDCl_3}$): $\delta$ 4.11 (br, $\mathrm{C_5}H_4$), 3.99 (br, Cp), 3.35 (br m, NHC$H_2$), 2.54 (br m, $CH_2\mathrm{C_5H_4}$), 2.19 (br m, COC$H_2$) 1.70 (br m, $\mathrm{CH_2}CH_2\mathrm{CH_2}$), 0.57 (m, $CH_2$Si), 0.07 (s, SiC$H_3$). $^{29}$Si{$^1$H} NMR ($\mathrm{CDCl_3}$): $\delta$ $-20.58$. IR (KBr): amide I, 1641 cm$^{-1}$; amide II, 1547 cm$^{-1}$. Anal. Calcd for $\mathrm{OH[C_{17}H_{23}NO_2SiFe]_{30}H}$: C, 57.05; H, 6.50; N, 3.91. Found: C, 55.95; H, 6.26; N, 3.68.

**Synthesis of Polymer 11.** This polymer was prepared by method A starting from 1,1′-bis($\beta$-aminoethyl)ferrocene (0.41 g, 1.50 mmol) and poly[(3-chlorocarbonyl)propylmethylsiloxane (0.2 g, ≈1.2 mmol of COCl) in toluene. A brown solid was isolated, which was insoluble in all the solvents tested, so it could neither be totally purified nor well characterized. Nevertheless, its IR spectrum indicated that the condensation reaction had taken place. IR (KBr): amide I, 1638 cm$^{-1}$; amide II, 1540 cm$^{-1}$.

## Results and Discussion

**Synthetic Approach.** Two general synthetic routes were explored for the incorporation of ferrocenyl moieties into silicon-containing polymer backbones through amide linkages. The first method consisted of exploiting the ability of (chlorocarbonyl)ferrocene and 1,1′-bis(chlorocarbonyl)ferrocene to undergo classical condensation reactions, with amine-functionalized siloxanes in the presence of a base to neutralize the acidic byproduct liberated in the reaction. This approach paralleled closely the synthetical procedure reported for a number of ferrocene-containing polyamides and polyesters.[14,19] Nevertheless, no similarly constructed siloxane polymers containing ferrocenylamide moieties in the backbone have been reported.[20] In the second approach, an organometallic moiety that chemi-

---

(17) Bachrach, A.; Zilkha, A. *Eur. Polym. J.* **1984**, *20*, 493.

(18) (a) Ohyanagi, M.; Kanai, H.; Katayama, Y.; Ikeda, K; Sekine, Y. *Polym. Commun.* **1985**, *26*, 251. (b) Ohyanagi, M.; Ikeda, K; Sekine, Y. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 795.

(19) Pittman, C. U., Jr. *J. Polym. Sci.* **1968**, *45*, 1687.

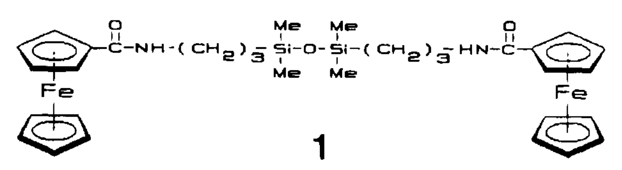
(20) A series of ferrocene-containing siloxane polymers was prepared from bis(dimethylamino)silane−disilanol condensations. See Patterson, W. J.; Manus, S. P.; Pittman, C. U. *J. Polym. Sci., Part A-1* **1974**, *12*, 837.

cally behaves as a Lewis base was allowed to react with an organosilane and a poly(methylsiloxane) functionalized with acid chloride groups. In this method, the key starting ferrocene monomers were ($\beta$-aminoethyl)ferrocene and 1,1′-bis($\beta$-aminoethyl)ferrocene. These monomers were selected because the amino functional group is two methylene units removed from the ferrocene nucleus. Previous works showed that the amine functionality must be essentially isolated from the cyclopentadienyl ring by at least two intervening methylene groups, in order to avoid any steric and electronic effects of the organometallic fragment which may retard the polymerization reactions.[15,21]

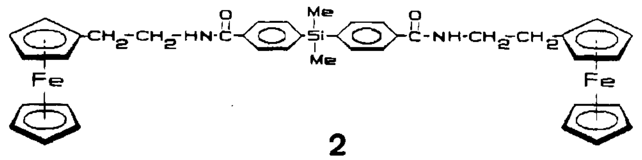
In both approaches, the polycondensation reactions were conveniently accomplished by either solution or interfacial techniques, and at ambient or low temperature, in contrast to earlier high-temperature organometallic condensation polymerizations, which frequently led to undesirable side reactions.[22,23] Both condensation approaches were successful, and provided access to an interesting series of ferrocene-containing poly(organosilane) and poly(methylsiloxanes), in which the amide-linked ferrocenyl moieties are incorporated in the polymer either as a part of the polymer backbone or as pendant side groups.

Similar condensations methods, starting from the monofunctionalized ferrocenes, are also a convenient way to prepare the corresponding model complexes.

**Synthesis, Characterization, and Electrochemistry of Dimeric Model Compounds.** The condensation reaction of 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane with 2 equiv of (chlorocarbonyl)ferrocene, in toluene solution, at room temperature, and in the presence of triethylamine as the base, affords the siloxanyl-bridged dimetallic model complex $[\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4C(O)NH(CH_2)_3Si(CH_3)_2\}]_2\text{-}O$ (**1**). The reaction was instantaneous and exothermic, and an orange precipitate was formed immediately. The purification of the reaction product was effected by column chromatography on silica, and the final compound **1**, was isolated as air-stable orange crystals. A similar condensation was performed by reacting ($\beta$-aminoethyl)ferrocene with dimethylbis(4-chlorocarbonylphenyl)silane in dichloromethane. This reaction was also completed in a few minutes, as was indicated by IR spectroscopy. The dimeric product $[\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4CH_2CH_2NHC(O)(C_6H_4)\}]_2SiMe_2$ (**2**), was successfully isolated after adecuate purification as a yellow crystalline solid. Compound **2** was also prepared by an aqueous interfacial condensation system. In this method, a suspension of ($\beta$-aminoethyl)ferrocene in deoxygenated water containing an excess of triethylamine, was found to form a yellow precipitate immediately on being shaken vigorously with 1 equiv of dimethylbis(4-chlorocarbonylphenyl)silane in dry benzene. After isolation and purification, elemental analysis and spectroscopic characterization data indicated that the yellow solid possesses the structure proposed for **2**. The above described reactions proceed in high yields, with no apparent side reactions. The dimetallic model compounds **1** and **2** were characterized by infrared spectroscopy, $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopies, mass spectrometry, and elemental microanalysis.



**1**



**2**

The infrared spectra of the model dimers agree with those of amide derivatives, exhibiting the characteristic N−H strech in the 3250−3320 cm$^{-1}$ range, and the amide I, amide II, and amide III bands at about 1635, 1540, and 1300 cm$^{-1}$ respectively.[24] $^1$H NMR data of **1** (in $CDCl_3$) and **2** (in $CD_3COCD_3$) are also consistent with the structures shown for compounds **1** and **2**. Both spectra showed a broad resonance corresponding to a secondary amide proton,[25] at 6.31 ppm in **1** and at 7.82 ppm in **2**, and the pattern of resonances characteristic of monosubstituted ferrocenyl derivatives, along with the proton resonances due to the organic groups attached to the silicon atoms, in the expected integrated ratio. In particular, the spectrum of compound **1** shows a sharp singlet at 4.21 ppm and two pseudotriplets corresponding to a AA′ system at 4.75 and 4.33 ppm while for **2** these resonances appear at 4.14, 4.13, and 4.05 ppm respectively. The downfield shift of the monosubstituted cyclopentadienyl ring protons in **1** is consistent with the electron-withdrawing effect of the amide group directly attached to the ferrocenyl moiety. The $^{29}$Si NMR spectra of **1** and **2** consist in both cases of a single resonance with chemical shifts in the expected regions of the spectrum.[26] Thus, the M-type silicon atom[27] in **1** gives a resonance at 7.62 ppm, and the dimethyldiphenyl-substituted silicon atom in **2** appears at −7.41 ppm. The FAB mass spectral analysis for **1** and **2** showed the molecular ions at *m/z* 672 and 722 respectively as the base peaks, together with numerous informative peaks assignable to reasonable fragmentation products (see Experimental Section).

The electrochemical properties of the dinuclear model compounds **1** and **2** were studied in dichloromethane and acetonitrile solutions containing 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, at platinum and glassy carbon electrodes. The cyclic voltammograms of **1** and **2** show a single reversible oxidation process with the production of soluble stable cations. The peak current is linearly proportional to the square root of the scan rate $\nu$, the ratio of the cathodic to anodic current, $i_{pc}/i_{pa}$, is essentially equal to unity, and $E_p$ is independent of the scan rate. Formal potential values are indicated in Table 1, and show that the oxidation of the ferrocenyl units in **1** occurs at a potential significantly more positive (by about 200 mV) than the corresponding process in dimer **2**. This is due to the strong electron-withdrawing effect of the carbonyl group on the ferrocenyl moiety when bound

---

(21) (a) Trifan, D. W.; Backsai, R. *Tetrahedron Lett.* **1960**, *1*, 1. (b) Watts, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E., Eds.; Pergamon Press: New York, 1982; Vol. 8, p 1052. (c) Gonsalves, K.; Zhan-ru, Lin; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 3862. (d) Tenhaeff, S. C.; Tyler, D. R. *Organometallics* **1992**, *11*, 1466.

(22) Carraher, C. E. Organometallic Polymers In *Interfacial Synthesis, Vol. II. Polymer Applications and Technology;* Millich, F., Carraher, C. E., Jr., Eds.; Marcel Dekker, Inc.: New York, 1977.

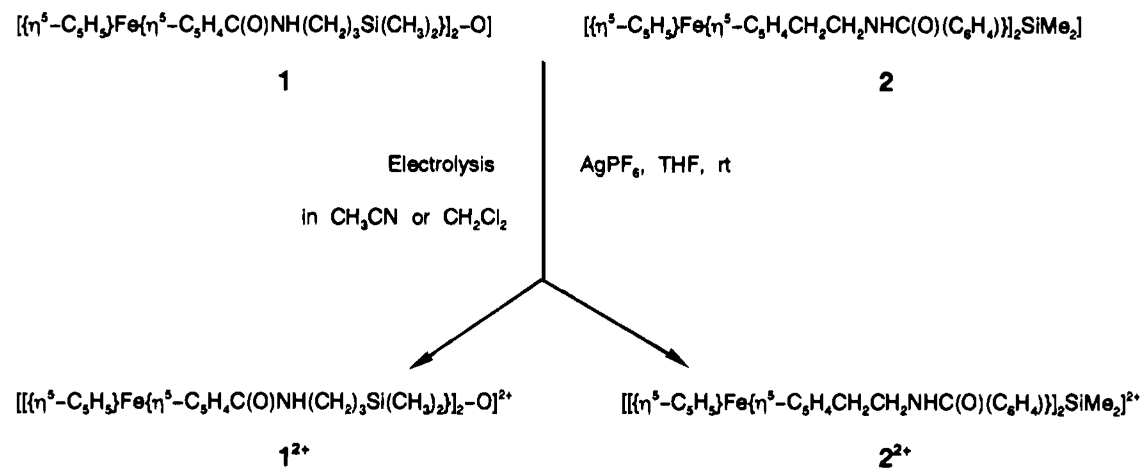
(23) Neuse, E. W.; Rosenberg, H. *Metallocene Polymers*; Marcel Dekker: New York, 1970.

(24) *Introduction to Infrared and Raman Spectroscopy*, 3rd ed.; Colthup, N. B., Daly, L. H., Wiberley, S. E., Eds.; Academic Press, Inc.: San Diego, 1990.

(25) (a) Friebolin, H. *Basic One- and Two-Dimensional NMR Spectroscopy*; VCH: Weinheim, 1991. (b) Sanders, J.; Hunter, B. *Modern NMR Spectroscopy. A Guide for Chemists*; Oxford University Press: New York, 1991.

(26) *The Analytical Chemistry of Silicones*; Smith, A. L., Ed ; John Wiley & Sons, Inc.: New York, 1991.

(27) In siloxane chemistry the symbols, M, D, T, and Q are used to represent framework silicon atoms which possess 3, 2, 1, and 0 organyl substituents, respectively.



(1)

**Table 1.** Formal Potentials for the Siloxanyl and Organosilyl Ferrocene Model Compounds and Polymers[a]

| compd | solvent | $E_{1/2}$ (V) [$\Delta E_p$ (mV)] | compd | solvent | $E_{1/2}$ (V) [$\Delta E_p$ (mV)] |
|---|---|---|---|---|---|
| **1** | $CH_3CN$ | +0.60 [65] | **4** | $CH_2Cl_2$ | +0.65 [65] |
| | $CH_2Cl_2$ | +0.61 [80] | **5** | THF | +0.39 [85] |
| **2** | $CH_3CN$ | +0.36 [65] | **6** | $CH_2Cl_2$ | +0.63 [70] |
| | $CH_2Cl_2$ | +0.38 [75] | **7** | $CH_2Cl_2$ | +0.62 [70] |
| **3** | $CH_3CN$ | +0.59 [60] | **9** | $CH_2Cl_2$ | +0.63 [75] |
| | $CH_2Cl_2$ | +0.60 [80] | **10** | $CH_2Cl_2$ | +0.35 [65] |

[a] Measured in 0.1 M TBAH, at a scan rate = 100 mV/s and using a platinum disk electrode. The $E_{1/2}$ values are relative to SCE; ±0.01 V.

directly to the cyclopentadienyl ring, making **1** more difficult to oxidize. This feature agrees with the above commented $^1H$ NMR spectral data.

Bulk coulometry of **1** and **2** carried out in $CH_2Cl_2$ or $CH_3CN$ solutions, at $E_{appl}$ ca. 100 mV more positive than the respective anodic potentials (Pt mesh, ambient temperature) indicates a two-electron exchange, and transformed **1** and **2** into the dicationic species $[1^{2+}][PF_6^-]_2$ and $[2^{2+}][PF_6^-]_2$ whose solutions are deep blue (eq 1). Reelectrolysis quantitatively regenerated the starting neutral dinuclear compounds. On the other hand, differential pulse voltammetry (DPV) measurements for **1** and **2** gave only one wave, suggesting that oxidation of the two ferrocenyl moieties occurred at the same potential. The described electrochemical results indicate that the two ferrocenyl moieties in **1** and **2** are essentially noninteracting redox centers.[28]

In order to attempt to generate and characterize solutions of the two-electron oxidized products of dimers **1** and **2**, in situ infrared spectroelectrochemical techniques were applied. Figure 1 shows the spectral changes in the 1800–1500 $cm^{-1}$ region that accompany the controlled-potential oxidation of the dimetallic compound **1**, in $CH_2Cl_2$/TBAH, in the thin layer cell, at room temperature. With the application of an oxidizing potential, the amide I $\nu(C{=}O)$ band at 1643 $cm^{-1}$, due to the neutral compound **1**, decreases in intensity while a new carbonyl band grows in isosbestically at 1669 $cm^{-1}$, indicating a clean conversion. The shift to a higher frecuency in this $\nu(C{=}O)$ band is produced because the oxidation of the ferrocenyl moieties in **1**, inductively withdraws electron density from the amide groups directly attached to the cyclopentadienyl ring, and thus increases the strength of the C=O bonds. The observed shift upon oxidation agrees with the trends found in recent infrared spectroelectrochemical studies on ferrocenecarboxylate derivatives, as a result of the generation of ferrocenium groups.[29]

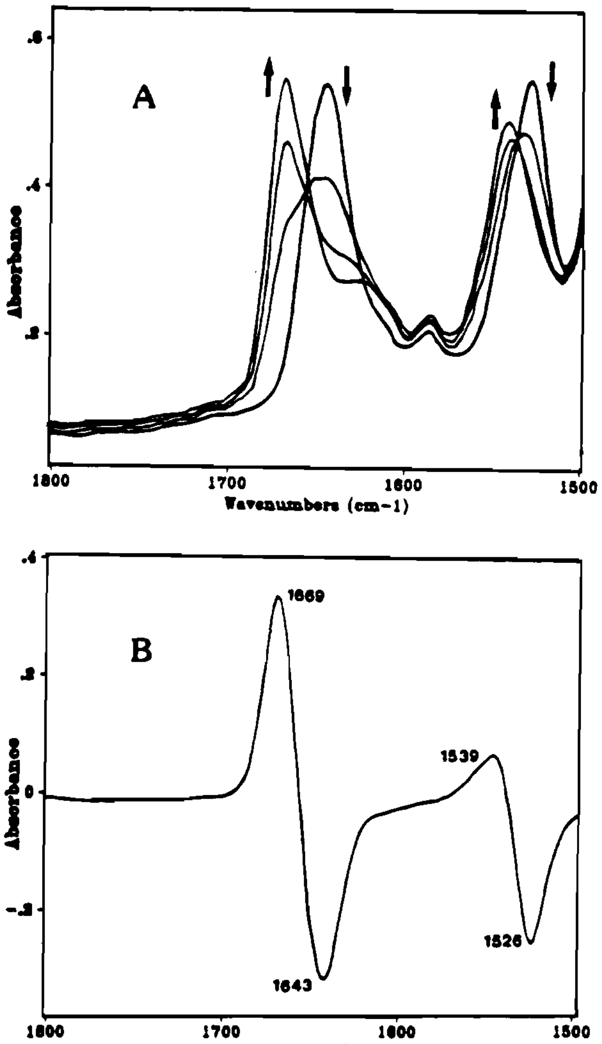


**Figure 1.** (A) Infrared spectral changes observed upon oxidation of $[\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4C(O)NH(CH_2)_3Si(CH_3)_2\}]_2\text{-}O$ (**1**) in $CH_2Cl_2$/TBAH at +0.9 V *vs* Ag pseudoreference electrode in the spectroelectrochemical cell. (B) FTIR absorbance difference spectra of the starting dimer and the electrooxidation product.

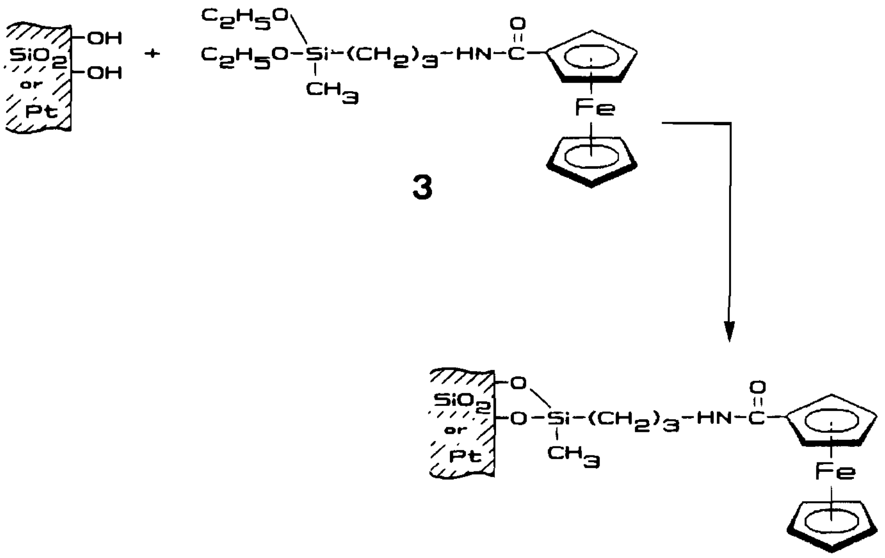
A similar spectroelectrochemical study was performed with the model dimer **2**, under the same experimental conditions. In this case, no changes in the IR spectrum were noted in the amide I region over several minutes of electrolysis. Nevertheless, after

---

(28) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* **1978**, *100*, 4248.

(29) Popenoe, D. D.; Deinhammer, R. S., Porter, M. D. *Langmuir* **1992**, *8*, 2521.

**Scheme 1**



this time the initial orange neutral solution was oxidized to the typical blue solution of the ferrocenium cations. The lack of shift in this $\nu$(C=O) band can be explained because in **2**, the two ferrocenyl moieties are removed from the amide groups by a two carbon chain, which largely masks any electronic influence due to the generation of the ferrocenium groups.

The dicationic species $[\mathbf{1}^{2+}][\mathrm{PF_6}^-]_2$ and $[\mathbf{2}^{2+}][\mathrm{PF_6}^-]_2$ were also chemically prepared by oxidation with equimolar amounts of silver hexafluorophosphate, in tetrahydrofuran (THF) solution, at room temperature (eq 1).

**Modification of Platinum and Silica Surfaces with Amide-Linked Ferrocenyl Moieties.** It was well-established that the attachment of organosilane derivatives to a surface oxide via siloxane bonds represents one of the more versatile methods of surface modification.[30] Because of the presence of oxide surface layers on various electrode materials, such as Pt, Si, C, and indium tin oxide (ITO), this method has proved suitable to electrode functionalization.[31]

In order to try surface attachment of ferrocenyl derivatives via siloxane linkages, we synthesized a monomeric compound containing ethoxysilyl groups $\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4C(O)NH(CH_2)_3SiCH_3(OCH_2CH_3)_2\}$ (**3**), and next we have studied the immobilization of **3** on surfaces of platinum electrodes and silica particles. The results are consistent with the covalent bonding between the ferrocenylamide moieties and the surfaces via siloxane linkages, as is illustrated in Scheme 1.

Compound **3** was prepared by reacting (chlorocarbonyl)ferrocene with (3-aminopropyl)methyldiethoxysilane, under solution reaction conditions similar to those used to prepare the related dimer **1**. In this case, the separation of the desired compound from the triethylamine hydrochloride byproduct was succesfully accomplished by column chromatography by using special silanized silica in order to avoid the facile reaction of the ferrocenyl derivative with the silica surface hydroxylic groups. The target monomer **3** was finally isolated pure as orange crystals and was structurally characterized by multinuclear NMR spectroscopy and elemental analysis, and the resulting data are consistent with the proposed structure.

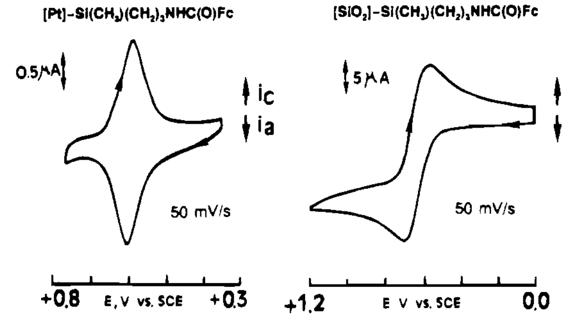


**Figure 2.** Cyclic voltammograms of (A) a Pt disk-electrode silanized with monomer $\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4C(O)NH(CH_2)_3SiCH_3(OCH_2CH_3)_2\}$ (**3**) in $CH_3CN$/0.1 M TBAH and (B) a glassy carbon disk-electrode derivatized with $[SiO_2]Si(CH_3)(CH_2)_3NHC(O)Fc$ (Fc = $\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4\}$) in $CH_3CN$/0.1 M TBAH.

The solution electrochemical behavior of **3** was analyzed via cyclic voltammetry using $CH_3CN$ and $CH_2Cl_2$ solutions with 0.1 M TBAH. At ca. +0.6 V *vs* SCE, **3** undergoes a diffusion-controlled, reversible one-electron oxidation (confirmed by coulometry).

In addition, we have studied the electrochemistry of **3** immobilized on platinum electrode surfaces. The Pt electrodes to be derivatized, pretreated to have an oxide layer,[32] were immersed in a dry toluene solution of the monomer **3**. The electrodes were removed, and after a thorough rinsing with $CH_3CN$, they were examined by cyclic voltammetry in $CH_3CN$/0.1 M TBAH. As shown in Figure 2A, the cyclic voltammogram of a derivatized electrode reveals a persistent redox wave at a formal potential value of $E_{1/2} = +0.58$ V *vs* SCE, which is virtually identical to that of the nonattached monomer **3** in $CH_3CN$ solution (Table 1). The amount of material bound to the electrode surface ($\Gamma$), is determinated by measuring the amount of charge associated with the oxidation of the redox centers, by integrating the area under the oxidation wave,[31,33] and was found to be $4.7 \times 10^{-10}$ mol/cm$^2$. The surface wave exhibits the symmetry, the small peak potential separation ($\Delta E_p \approx 5-15$ mV at $v \leq 100$ mV/s), and the expected linear relationship of peak current with potential sweep rate characteristic of a surface-confined reversible redox couple.[31,33]

On the other hand, monomer **3** is a suitable organometallic moiety to be also attached to inorganic supports as silica,

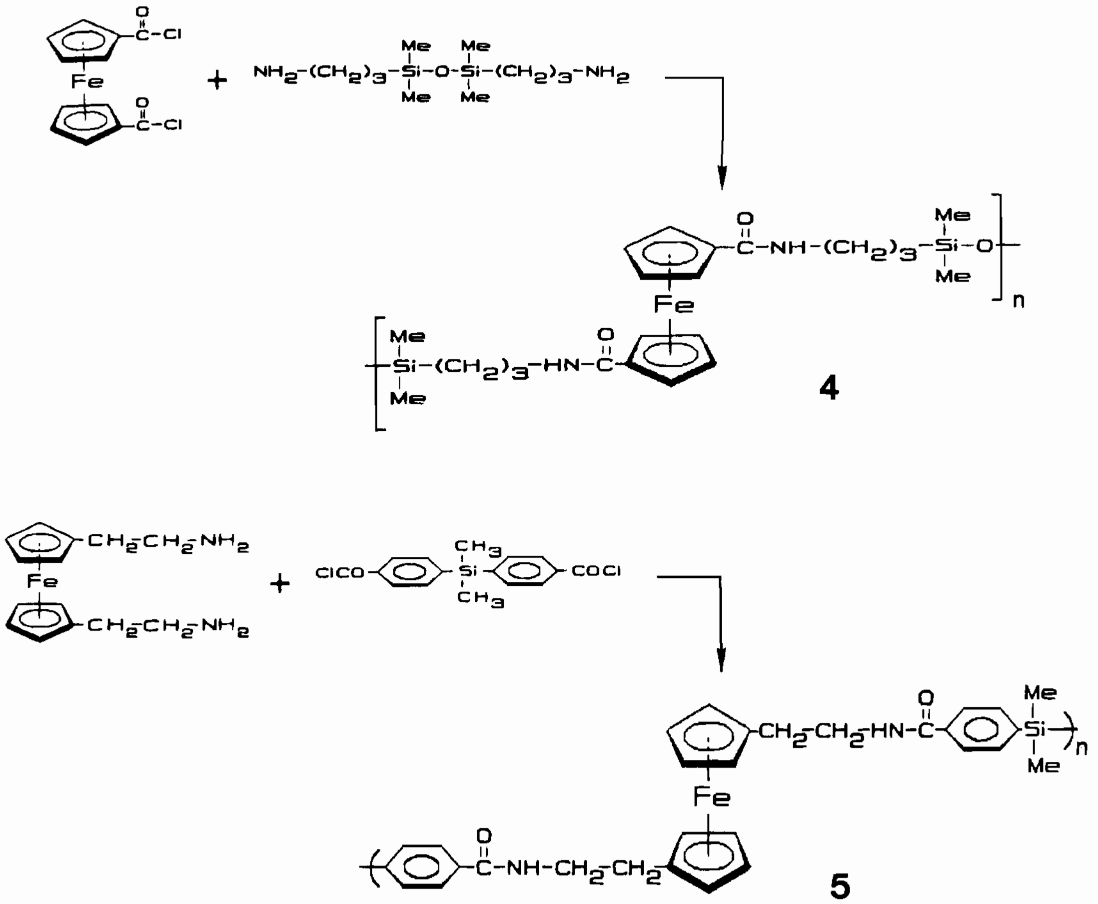
---

(30) (a) *Silanes Surfaces and Interfaces*; Leyden, D. E., Ed.; Chemically Modified Surfaces 1; Gordon and Breach Science Publishers: New York, 1986. (b) Li, D.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7389. (c) Deschler, U.; Kleinschmit, P.; Panster, P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 236.

(31) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1984; Vol. 13.

(32) Lenhard, J. R.; Murray, R. W. *J. Electroanal. Chem.* **1977**, *78*, 195.

**Scheme 2**



alumina, or zeolites, due to the reactivity of the ethoxysilyl substituents toward surface OH groups of these inorganic materials. Reaction of $SiO_2$ gel directly with **3**, in a toluene solution at 85−90 °C results, after appropriate isolation, in an orange material. The primary identification of this derivatized material was based on the IR spectrum, which shows the two strong amide I and amide II bands at 1634 and 1541 $cm^{-1}$, in close agreement with those of the corresponding homogeneously dissolved monomer **3**. Analysis of the derivatized silica shows $7.32 \times 10^{-4}$ mol/g of organometallic units. In order to provide additional characterization of **3** immobilized on $SiO_2$ surfaces, $[SiO_2]-Si(CH_3)(CH_2)_3NHC(O)Fc$ (Fc = $\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4\}$), we utilized CP/MAS solid-state NMR spectroscopy. The observed $^{13}C$ resonances were assigned by comparison with those measured for compound **3** in $CDCl_3$ solution. As expected, an intense peak was observed at ≈70 ppm due to the carbons on the cyclopentadienyl rings. The broad resonance in the 6−0 ppm range is assigned to the carbons bonded to the silicon atom, the peak due to the central methylene appears at ≈22 ppm, and at ≈40 ppm the resonance corresponding to the carbon adjacent to the amide group. In addition, a resonance is observed at 171 ppm, which is attributable to the carbon atom of the amide group.

We have also studied the electrochemical behavior of electrodes modified with films of monomer **3** immobilized on silica. Figure 2B shows the cyclic voltammetry, in $CH_3CN$/0.1 M TBAH, of a glassy carbon-disk electrode modified with $[SiO_2]-Si(CH_3)(CH_2)_3NHC(O)Fc$ following the procedure described in the Experimental Section. The $SiO_2$−ferrocenylamide attached species are electroactive, as a reversible system appears at $E_{1/2}$ = +0.62 V *vs* SCE which can be adscribed to the $[SiO_2]-Si(CH_3)(CH_2)_3NHC(O)Fc/[SiO_2]-Si(CH_3)(CH_2)_3NHC(O)Fc^+$ couple, and that unequivocally establishes the attachment of the amide-linked ferrocenyl moieties to the $SiO_2$ surface. The surface coverage of electroactive material was determined to be $2.06 \times 10^{-8}$ mol/cm$^2$. The peak current ratio $i_{pc}/i_{pa}$ is ca. 1, and the peak potential separation $\Delta E_p$ is ca. 120 mV at 50 mV/s (without *iR* compensation), and increases with increasing scan rate. This value of $\Delta E_p$ is significantly larger than those found for the silanized electrode described above, and can be attributed to kinetic limitations in charge transport through this type of film.[31]

**Polymer Synthesis and Characterization.** A methylsiloxane polymer $[-Si(CH_3)_2(CH_2)_3NHC(O)(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)C(O)NH(CH_2)_3Si(CH_3)_2O-]_n$ (**4**), in which amide-linked ferrocenyl moieties are fixed on the main polymer chain, has been prepared by polycondensation of 1,1′-bis(chlorocarbonyl)ferrocene with 1,3-bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane and triethylamine as base (Scheme 2). Likewise, treatment of 1,1′-bis(β-aminoethyl)ferrocene with dimethylbis(4-chlorocarbonylphenyl)silane yielded the polyamide $[-C_6H_4C(O)NHCH_2CH_2(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_4)CH_2CH_2NHC(O)C_6H_4Si(CH_3)_2-]_n$ (**5**), with a backbone consisting of alternating dimethyldiphenylsilyl groups and ferrocenyl units bonded through amide linkages (Scheme 2). In this case, since the difunctional starting ferrocene monomer has the reactive groups two methylene units removed from the metallocenyl moiety, steric effects are reduced and the instability found in polymers of α-functional ferrocenes, due to the α-ferrocenyl carbonium ion stability, is avoided.[34]

---

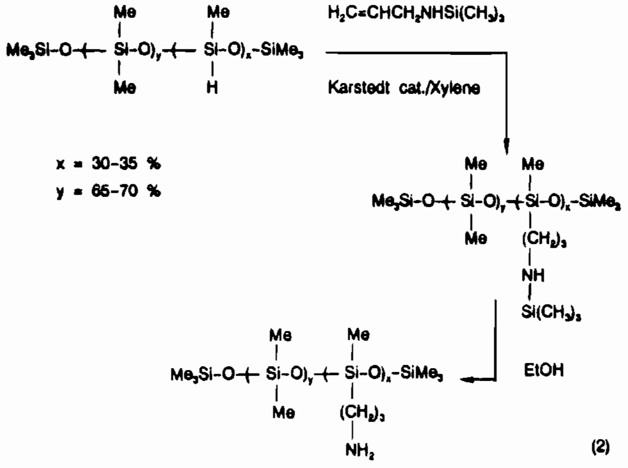
(33) (a) Abruña, H. D. Electrode Modification with Polymeric Reagents. In *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Dekker: New York, 1988; Vol 1. (b) *Molecular Design of Electrode Surfaces*; Murray, R. W., Ed.; Techniques of Chemistry XXII; Wiley: New York, 1992.

The polymerization reactions were accomplished by solution and interfacial techniques, at ambient or low temperatures. In both cases, imide branching formation, due to a possible side reaction of the acid chloride with the amide groups, was minimized by the use of relatively dilute reaction conditions, rapid reactant addition and rapid stirring.[35] Generally, in the aqueous interfacial polycondensations using toluene as the organic phase and triethylamine as base, polyamide formation takes place immediately. Likewise, as in the case of the model reactions, solution polycondensations have also proved to be effective and very rapid. After isolation, polymers **4** and **5** were purified by treatment of the reaction products with acetonitrile, followed by repeated reprecipitations from concentrated dichloromethane or tetrahydrofuran solutions of the polymers into a large volume of acetonitrile or hexanes, in order to remove possible unreacted starting materials or cyclization products. The polyamides **4** and **5** were isolated as yellow-orange solid materials.

Structural characterization of polymers **4** and **5** was achieved by infrared spectroscopy, $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopy, and elemental analysis, and the number-average molecular weights, ($M_n$), were determined by vapor pressure osmometry. The spectroscopic data are nearly identical to those of the model dimers **1** and **2**, with the exception of some broader $^1$H NMR resonances. Both polyamides show the characteristic infrared absorption corresponding to the N−H stretch and the amide I, II, and III bands, in the same regions as those observed for the respective model dimers. The $^1$H NMR spectra (in $CDCl_3$) show two broad resonances for the two sets of cyclopentadienyl protons at 4.52 and 4.38 ppm for **4**, and at 4.08 and 3.99 ppm for **5**, together with the resonances assigned to protons in the organic groups attached to silicon. The ratio of the resonances was as expected. Both $^{29}$Si NMR spectra consist of a single resonance, that in the case of **4** was detected at 7.63 ppm, in the region of the M-type silicon atoms, whereas for polymer **5**, with silicons bonded to phenyl groups, the resonance was observed at −7.39 ppm. Elemental analysis data for polymers **4** and **5**, are in agreement with the assigned structures, although the results for the carbon are slightly low values. Similar problems were found by Manners and co-workers in poly(ferrocenylsilanes) and were attributed to an incomplete combustion, which can be due to the formation of ceramic products at elevated temperatures.[36] Further evidence for this feature came from the thermal analysis of our polymers. The polyamides **4** and **5** appear stable to the atmosphere and form orange or amber free-standing films when cast from solution using tetrahydrofuran or dichloromethane as solvents.

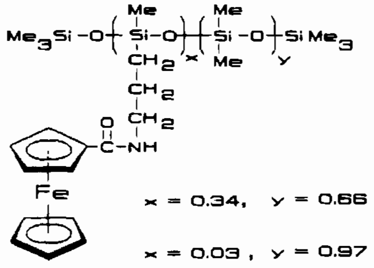
On the other hand, an alternative method we have used for incorporating ferrocene molecules along siloxane polymer backbones through amide linkages, involves the use of poly(methylsiloxanes) containing side chains functionalized with chlorocarbonyl and amine groups, capable of reacting subsequently with the suitable functionally-substituted ferrocene monomers. In order to study the effect of the variations in the loading of ferrocenyl units on the properties of the polymers, a series of derivatized polymeric supports were selected.

Methylaminopropyl(30−35%)dimethylsiloxane(65−70%) copolymer was prepared by a modification of methylhydro(30−35%)dimethylsiloxane(65−70%), as indicated in eq 2.



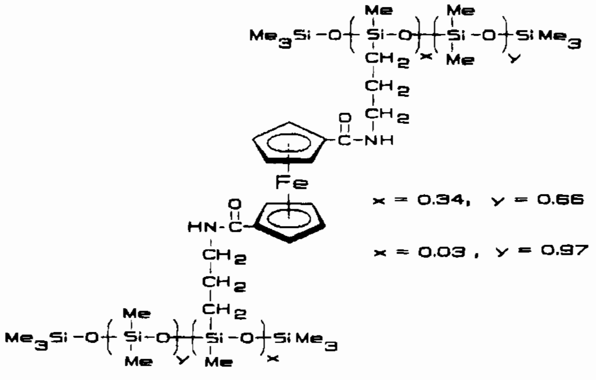
(2)

This support, as well as the comercially available methylaminopropyl(3−5%)dimethylsiloxane(97−95%) copolymer, were treated with (chlorocarbonyl)ferrocene and 1,1′-bis(chlorocarbonyl)ferrocene. The reactions were carried out following the solution or interfacial procedures previously described, and typically gave good yields. After appropriate workup, the new ferrocene-containing polymers **6**−**9** were isolated. These are siloxane copolymers with different *x*:*y* ratios, in which the amide-linked ferrocenyl moieties are randomly distributed along the flexible methylsiloxane backbones. Their spectroscopic data are consistent with the proposed structures. $^1$H NMR spectra, together with elemental analyses were important for estimation of the degree of ferrocene substitution. For **6** and **7**, satisfactory results were obtained when integration of the ferrocenyl and methyl protons was used. The results indicated that all the pendant amine groups in the siloxane chains have been derivatized, and that these ferrocenyl-substituted copolymers have approximate *x*:*y* ratios of 34:66 for **6**, and 3:97 for **7**.



**6**

**7**



**8**

**9**

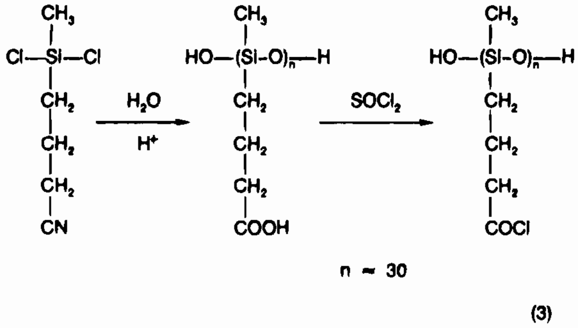
On the other hand, a poly(methylsiloxane) containing chlorocarbonyl groups in all the side chains was synthesized according to the step reactions outlined in eq 3, starting from

---

(34) Pittman, C. U.; Rausch, M. D. *Pure Appl. Chem.* **1986**, *58*, 617.

(35) Sekiguchi, H.; Coutin, B. Polyamides. In *Handbook of Polymer Synthesis. Part A*; Kricheldorf, H. R., Ed.; Marcel Dekker, Inc.: New York, 1992; pp 807−915.

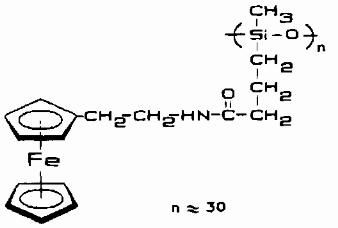
(36) (a) Foucher, D. A.; Ziembinski, R.; Tang, B.; MacDonald, P. M.; Massey, J.; Jaeger, C. R.; Vancso, G. J.; Manners, I. *Macromolecules* **1993**, *26*, 2878. (b) Tang, B. Z.; Petersen, R.; Foucher, D. A.; Lough, A.; Coombs, N.; Sodhi, R.; Manners, I. *J. Chem. Soc., Chem. Commun.* **1993**, 523. See also ref 2b.



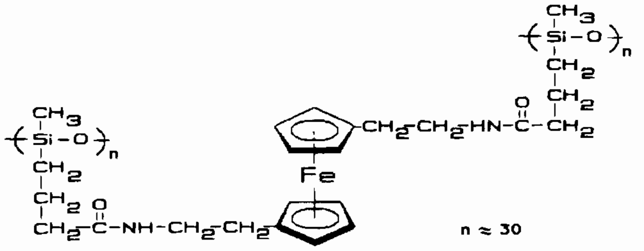
(3)

(3-cyanopropyl)methyldichlorosilane.

Due to the high concentration of $-C(O)Cl$ groups in this polysiloxane, condensation reactions with $NH_2$-functionalized ferrocene monomers were effected only under solution conditions, in order to prevent possible hydrolysis and decomposition. In the synthesis of the polymer $[[\{\eta^5\text{-}C_5H_5\}Fe\{\eta^5\text{-}C_5H_4CH_2CH_2NHC(O)CH_2CH_2CH_2\}]CH_3SiO-]_n$ (**10**), poly[(3-chlorocarbonylpropyl)methylsiloxane] was allowed to react with an excess of ($\beta$-aminoethyl)ferrocene, in dichloromethane solution, and in the presence of triethylamine as the acid acceptor. Complete condensation of the C(O)Cl sites along the backbone occurred, even under mild reaction solution conditions. After appropriate purification, integration of the $^1H$ NMR spectrum together with elemental analysis indicated that polymer **10** represents an example of a poly(methylsiloxane) that has all side chains coordinated to ferrocenyl moieties through amide linkages.



**10**



**11**

It is interesting to note the different physical properties observed for the synthesized polymers, which can be understood in terms of the influence of the backbone structure, together with the effect of the side groups. The polyamides **4** and **5**, with ferrocenyl units in the main polymer chain are amorphous solids, less soluble than the respective models **1** and **2**. However, these polymers are soluble enough in tetrahydrofuran or dichloromethane to be characterized, being insoluble in solvents such as acetonitrile and hexane. On the other hand, the polymers **7** and **9**, with a very low loading of pendant ferrocenyl units attached to a flexible methylsiloxane copolymer backbone, are viscous materials, highly soluble in tetrahydrofuran or dichloromethane, and somewhat soluble in hexane. In contrast, polymers **6**, **8**, **10**, and **11**, with a higher degree of ferrocene substitution, were isolated as shiny solids and show a much more limited solubility. Moreover, **8** and **11** swelled without dissolving on attempted dissolution in $CH_2Cl_2$ or THF. Similar behaviors have been observed in some organometallic polymers[37] and may be the result of an ordered packing of the chains which could generate microcrystalline domains, and reduce the solubility.[1f] In addition, the very insoluble nature of polymers **8** and **11** in all the organic solvents tested suggests a possible cross-linking, via the bonding of the ferrocenyl moieties to two different siloxane chains. Because of this insolubility, a complete structural characterization and solution electrochemical studies of these polymeric materials are precluded.

The thermal behavior of polymers **4**–**11** was examined with the aid of thermal gravimetric analysis (TGA), derivative thermogravimetry (DTG), and differential thermal analysis (DTA). The samples were heated at a ramp rate of 10 °C/min, under nitrogen and air atmospheres, in the temperature range 25–850 °C. Under an inert atmosphere, the decomposition starts at about 150 °C for all the polymers, and beyond 800 °C a leveling off in the weight loss is observed. TGA analysis indicated that the polymers undergo the major decomposition between 370 and 550 °C. The weight losses recorded up to the end of this range correspond to 40–58%. DTA data show that these weight losses correspond to endothermic effects. Under an air atmosphere, a strongly exothermic process was observed for polymer **5** just before the onset of weight loss. This process occurred without a corresponding change in the weight of the samples, which indicates that an exothermic rearrangement of the polymer may have occurred. We have also observed this effect in the thermoanalytical study of related polymers.[7] In the case of **4** and **5**, under $N_2$ and air atmospheres, the major weight losses are faster than those found in the other polymers. Potentially, the synthesized ferrocene-containing organosilicon polymers could be pyrolytic precursors to iron silicon carbide ceramics.[4,36] For this reason, the residues obtained via their pyrolysis under a nitrogen stream at 700 °C, which present magnetic properties, were analyzed by scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) analysis. These results, together with those of related polymers[5] will be presented separately.

**Electrochemistry of Polymers.** The electrochemistry of the synthesized polymers was studied in solution and confined to the electrode surface.

**(a) Solution Studies.** The electrochemical behavior of polymers **4**–**7**, **9**, and **10**, dissolved in dichloromethane, tetrahydrofuran, or dimethylformamide, containing 0.1 M TBAH, was studied by cyclic voltammetry, at platinum or glassy carbon electrodes. Each one of the polymers exhibits a single reversible oxidation process, and the $E_{1/2}$ values (obtained in $CH_2Cl_2$ or THF) are summarized in Table 1. The oxidation potentials of polymers **4**, **6**, **7**, and **9** are more positive than those of polymers **5** and **10** in agreement with the results mentioned above for the dimetallic compounds **1** and **2**. The detection of single reversible oxidation waves indicates that in these polymers the iron centers are essentially noninteracting.[28] The electrochemistry of **4** and **5**, with electroactive ferrocenyl moieties fixed in the main polymer chain, is fully consistent with the electrochemical results obtained for the respective dimetallic model complexes **1** and **2**. Nevertheless, the oxidation of these polymers is markedly different from that observed by Manners[2] and Diaz and Pannel[3a] in related poly(ferrocenylsilanes), for which two reversible oxidation waves have been detected by cyclic voltammetry, which has been interpreted in

---

(37) See: Allcock, H. R.; Dembek, A. A.; Klingenberg, E. H. *Macromolecules* **1991**, *24*, 5208 and references cited therein.

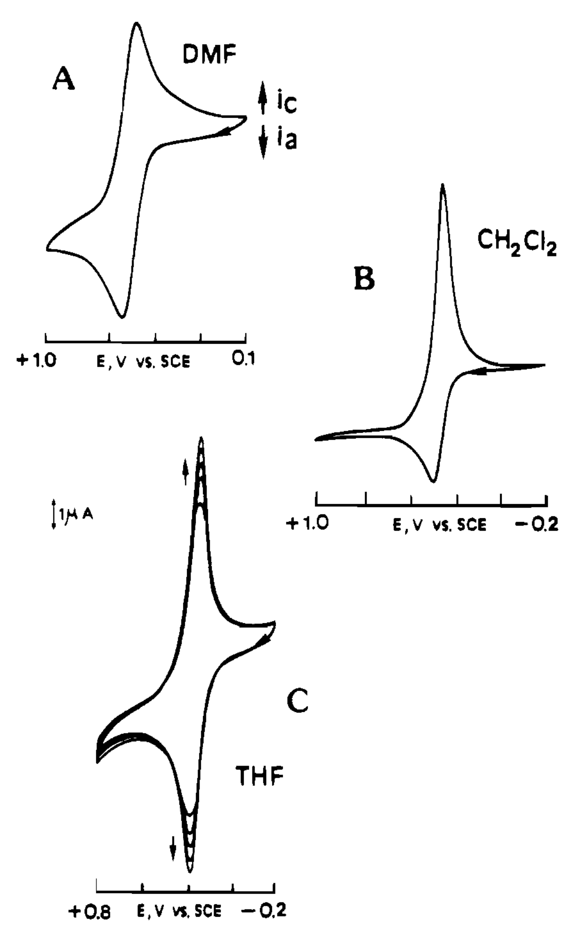


**Figure 3.** Cyclic voltammograms of polymer **10** at a Pt disk-electrode in solutions of (A) DMF/0.1 M TBAH, (B) $CH_2Cl_2$/0.1 M TBAH, and (C) THF/0.1 M TBAH, consecutive scans. (The scan rate was 50 mV/s.)

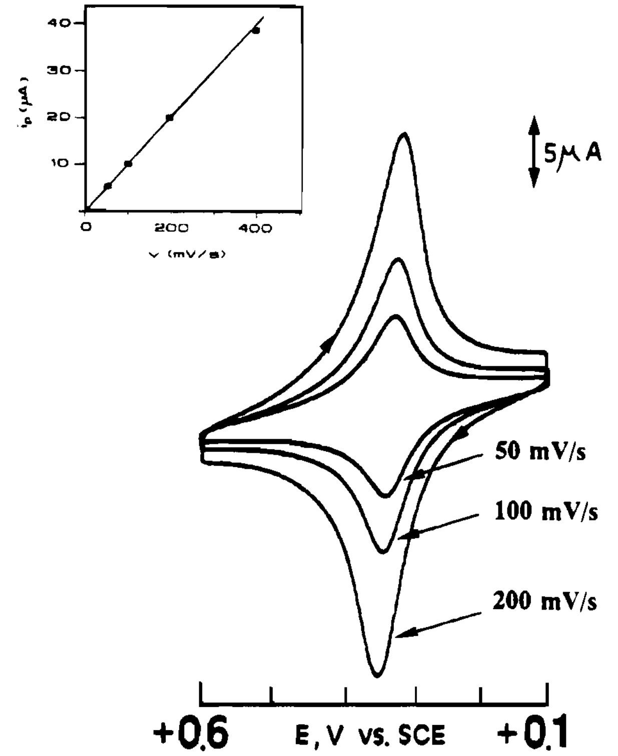


**Figure 4.** Cyclic voltammograms at 50, 100, and 200 mV/s in $CH_3CN$/0.1 M TBAH, for a Pt disk-electrode modified with an electrodeposited film of polymer **10**. Inset: plot of peak current *vs* sweep rate.

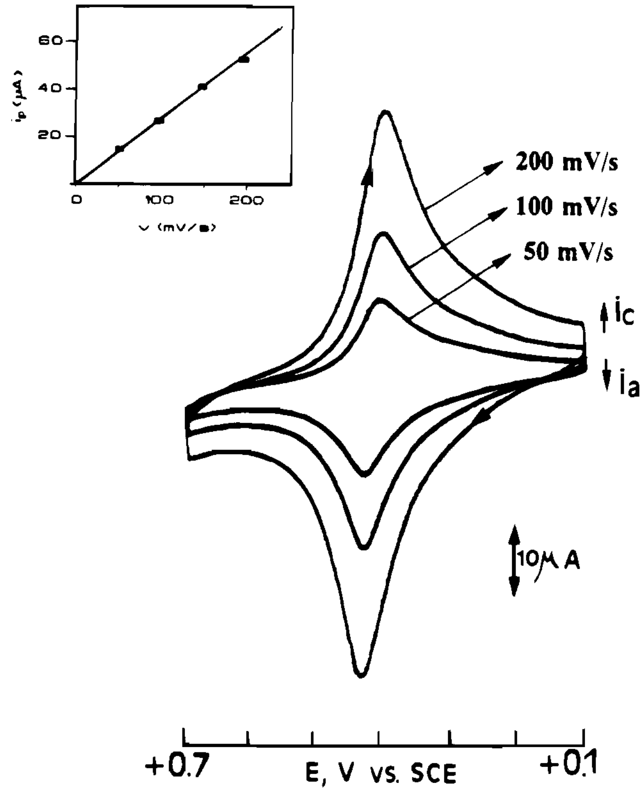


**Figure 5.** Cyclic voltammograms of a film of polyamide **5**, evaporatively deposited on a Pt disk-electrode, measured in $CH_3CN$/0.1 M TBAH. Inset: plot of peak current *vs* sweep rate.

terms of cooperative interactions between the iron centers. Because in our polymers **4** and **5** the redox-active ferrocenyl centers are separated from one another by large silicon-containing chains with insulating organic units, cooperative interactions are hindered.

It is worth noting that the solution redox behavior of the polymers studied here, appears to be sensitive to the polymer structure. Oxidation and reduction in $CH_2Cl_2$, THF, or DMF solutions with 0.1 M TBAH, does not affect the solubility of the polyamides **4** and **5**. The cyclic voltammograms have the characteristics of one-electron, reversible, Nernstian redox couples, and no increase of the peak current upon continuous scanning was detected. Therefore, **4** and **5** do not appear to precipitate when present as oxidized polymers. In contrast, for poly(methylsiloxanes) **6**, **7**, **9**, and **10**, which possess electroactive pendant ferrocenyl groups, changes in solubility with the change in the oxidation state in the ferrocene units, were observed. Figure 3 shows the effects of the solubility properties of polymer **10** as a representative example. In DMF/0.1 M TBAH, both neutral and oxidized states of **10** are soluble, and the cyclic voltammogram is typical of reversible redox couples. In $CH_2Cl_2$ and THF solutions, although the anodic wave has the form required if transport to electrode is controlled by diffusion, the cathodic wave does not. The shape of the reduction peak is characteristic of redox couples in which the oxidized form is insoluble and the reduced form is soluble, that is a stripping peak. In addition, upon continuous scanning, in either THF or $CH_2Cl_2$ there is an increase in the peak current with each successive scan (Figure 3C), which indicates that formation of an electroactive polymer film occurs on the electrode surface. Similar sharp cathodic stripping peaks were observed for **6**, **7**, and **9** in $CH_2Cl_2$ solution, although they are less pronounced than for **10**.

On the other hand, the cyclic voltammograms of **6**, **7**, and **10** in $CH_2Cl_2$ solution containing approximately the same molar amount of ferrocene units in all cases, have been recorded. For copolymer **7**, in which only ca. 3% of the siloxane backbone

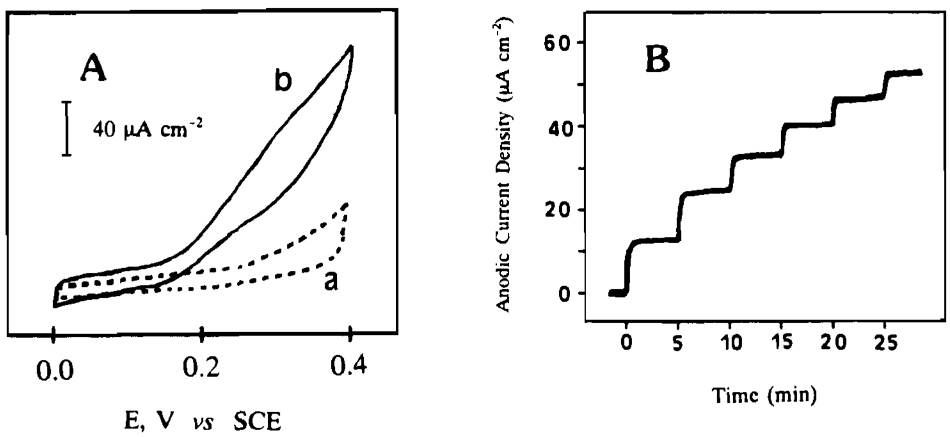


**Figure 6.** (A) Cyclic voltammograms for the polymer **10**/glucose oxidase carbon paste electrode at a scan rate of 5 mV/s, in pH 7.0 phosphate buffer (with 0.1 M KCl) solution with no glucose present (a) and in the presence of 0.1 M glucose (b). (B) Response of the carbon paste electrode to addition of glucose, at $E = +0.35$ V (*vs* SCE). Each increase in current density corresponds to the addition of 0.2 mL of 0.1 M glucose to the deoxygenated test solution (initial volume: 10 mL).

units are substituted with ferrocenyl moieties, the cathodic stripping current is smaller than for **6**, with ca. 34% of ferrocene units per siloxane chain. These observations suggest that the solubility of these ferrocene-substituted poly(methylsiloxanes) is also affected by the degree of ferrocene substitution. As the number of ferrocenyl moieties per siloxane chain increases, the solubility of the polymer is more affected by the state of charge in the ferrocene units. Consequently, the neutral fully ferrocene-substituted siloxane polymer **10** becomes the most insoluble of the studied polymers upon oxidation.

For polymers **6**, **7**, and **10**, which undergo oxidative deposition, the number of electrons in the process has been estimated by using the normal pulse voltammetry (NPV) technique.[38,39,40] From the normal pulse voltammograms, the values of the slopes of the plots $E$ *vs* $\log[(i_{\text{lim}} - i)/i]$ are in the range of 75–80 mV. Thus, all the ferrocenyl redox-active units in these polymers behave independently, and exchange electrons with the electrode in a wave characteristic of a one-electron process.

**(b) Modification of Electrodes with Ferrocene-Containing Siloxane and Organosilicon Polymer Films.** The chemical modification of platinum or glassy carbon electrode surfaces with the ferrocene polymers synthesized has been achieved by two methods.

For **6**, **7**, and **10**, the oxidative precipitation effects observed in their above described voltammetric studies have allowed the preparation of polymer-modified electrode surfaces. Films of these polymers were electrodeposited on the Pt surfaces by continuous scanning (at 50 or 100 mV/s) between ca. −0.2 and +1.0 V *vs* SCE, in degassed $CH_2Cl_2$ or THF polymer-containing solutions with 0.1 M TBAH. The electrodes thus coated were rinsed with $CH_2Cl_2$ or THF to remove any adhering solution and dried in air. The polymer films were characterized by cyclic voltammetry in fresh dichloromethane or acetonitrile solutions containing only supporting electrolyte. Figure 4 shows the voltammetric response of a Pt electrode modified with an electrodeposited film of **10**, as a representative example. A well-defined, single symmetric wave was observed at $E_{1/2} = +0.35$ V *vs* SCE, that is similar to the formal potential of the polymer in solution. The wave shape is independent of the scan rate and typical of a surface-confined reversible redox couple, with the expected linear relationship of peak current with potential sweep rate (Figure 4 inset). The peak to peak separation ($\Delta E_p$), varies from 2 mV at a scan rate of 10 mV/s to 10 mV at 100 mV/s, which suggests that the rate of electron transfer is rapid on the time scale. The coverage of the polymer film can be controlled with the scan number and for the studied example was found to be $7.5 \times 10^{-10}$ mol/cm$^2$. The value of the full width at half-maximum ($\Delta E_{\text{FWHM}}$) is about 110 mV at 20 mV/s and is larger than $90.6/n$ ($n$ = number of electrons transferred per molecule), which is the expected value for surface-confined redox species.[31,33] This larger value can be attributed to repulsive interactions between the electroactive ferrocenyl sites attached to the electrode surface.[40] The Pt electrodes derivatized with electrodeposited films of polymer **10** have been found to be very stable in both $CH_3CN$ and $CH_2Cl_2$ solutions. Cyclic voltammetric scans between potentials where the electroactive material is reduced and oxidized can be carried out for over 4 h with no loss of electroactive species.

On the other hand, the redox properties of the polymers **4**–**7**, **9** and **10** have been also investigated as films evaporatively deposited on platinum and glassy carbon electrode surfaces, from polymer-containing solutions. For all polymers, this procedure provides good quality thin films, that can be electrochemically oxidized and reduced in acetonitrile solutions containing supporting electrolyte. This method is particularly useful for chemical modification of electrodes with polymers **4** and **5** in which oxidative precipitation effects were not observed. In several cases, the freshly deposited films exhibit asymmetric cyclic voltammograms, in which a very sharp anodic peak was observed. After several cyclic potential scans the cyclic voltammograms become more symmetric and finally the films exhibit reproducible, well-defined reversible redox responses, characteristic of surface confined redox couples (see Figure 5 as an example).

In the case of polymer **7**, with the highest number of dimethylsiloxane units, it is interesting to note the redox behavior of films evaporatively deposited on a glassy carbon electrode, which have been also studied in aqueous medium. Whereas in $CH_3CN$/TBAH, a well-defined redox response was obtained, in $H_2O$/KCl only background current was observed. The absence of redox wave for the ferrocenyl moieties observed in aqueous medium is probably related to the highly hydrophobic character of the poly(methylsiloxane) chains, which hinders the diffusion of water and electrolyte ions into the polymer film. However, when an anionic surface-active agent such as sodium *n*-dodecylbenzenesulfonate[41] was added to the polymer film,

---

(38) Bard, A. J., Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; Chapter 5.

(39) D'Silva, C.; Afeworki, S.; Parri, O. L.; Baker, P. K.; Underhill, A. E. *J. Mater. Chem.* **1992**, *2*, 225.

(40) Peerce, P.; Bard, A. J. *J. Electroanal. Chem., Interfacial. Electrochem.* **1980**, *114*, 89.

diffusion through the film is allowed, and well-defined anodic and cathodic waves, due to the redox reaction of the ferrocenyl moieties, appeared.

On the basis of the results described here, we anticipate that more detailed studies of the electrochemical properties of these polymers, and comparisons with those of related linear and cyclic polysiloxanes,[5] both in solution and confined to the electrode surface, will be of interest to study the relation between the structure of the polymer and the redox properties for ferrocene-containing siloxane materials.[42]

**Application of Ferrocenyl-Containing Poly(siloxanes) as Mediators in Amperometric Glucose Biosensors.** It has been shown that the high conformational flexibility of the siloxane backbones allows close contact between ferrocene mediators and the flavin adenine dinucleotide (FAD) redox centers of glucose oxidase.[9b-f] For this reason, in order to test the ability of the synthesized ferrocene-containing polysiloxanes to act as as mediating species in amperometric glucose biosensors, we have studied the efficiency of an enzyme/polymer modified carbon paste electrode. The electrode was prepared by dropping the carbon paste with the glucose oxidase, with polymer **10** as mediator, and the obtained voltammetric results are shown in Figure 6A. In the absence of glucose, the voltammogram exhibits a very low anodic current, because the oxidation of the ferrocenyl moieties (at about +0.35 V), is too small to be detected. The addition of glucose leads to the enhancement of the oxidation current, while no change in the reduction current is observed. This fact is indicative of enzyme-dependent catalytic reduction of the ferrocenium cations. Figure 6B shows a typical set of current responses to the addition of glucose, for the carbon paste electrode containing the enzime and polymer **10**. A rapid response, and an acceptable sensitivity of the electrode was observed. After addition of the glucose samples, the time needed to attain 95% of the steady-state current was less than 10 s. The obtained results appear to indicate that this electrode can act as an efficient glucose sensor.

**Acknowledgment.** Dr. Héctor D. Abruña (Cornell University) is acknowledged for helpful discussions. We thank the Dirección General de Investigación Científica y Técnica (DGICYT) (Proyect 93/0287) for financial support of this work.

IC941032O

---

(41) Kuwabata, S.; Hamamoto, T.; Yoneyama, H. *J. Electroanal. Chem.* **1991**, *301*, 165.

(42) The influence of the polymer structure and of the different amounts of ferrocene units, on the electrochemical behavior, for several ferrocene-containing polymers, has also been analyzed. See for example: (a) Albagly, D.; Bazan, G.; Wrighton, M. S.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 4150. (b) Crumbliss, A. L.; Cooke, D.; Castillo, J.; Wisian-Neilson, P. *Inorg. Chem.* **1993**, *32*, 6088. (c) Saraceno, R. A.; Riding, G. H.; Allcock, H. R.; Ewing, A. G. *J. Am. Chem. Soc.* **1988**, *110*, 980. (d) Saraceno, R. A.; Riding, G. H.; Allcock, H. R.; Ewing, A. G. *J. Am. Chem. Soc.* **1988**, *110*, 7254.