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Synthesis of Ferrocene and Cobaltocene Electrode Films by Electropolymerization and Their Spectral and Electrochemical Properties

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Electroreduction in acetonitrile solutions of $Fe(C_5H_4CH_2Cl)_2$ (**1**), $Fe(C_5H_4CCl{=}CHCHO)_2$ (**2**), $Fe(C_5H_5)(C_5H_4CCl{=}CHCHO)$ (**3**), and $[Co(C_5H_4CCl{=}CHCHO)_2]PF_6$ (**4**) led to deposition of stable electroactive films on glassy-carbon and indium tin oxide coated glass electrodes. Structure and characteristics of these films were investigated by FT-IR and UV-visible spectroscopy, scanning electron microscopy, and film thickness measurements. The volume concentrations of ferrocene sites and electroactive sites in the polymer $[Fe(C_5H_4CH_2-)_2]_n$ formed from 2 mM solution of **1** were estimated at 7.5×10^{-3} and 3.8×10^{-4} mol/cm^3, respectively. Scanning electron microscopy revealed a heterogeneity, probably coexistence of the electroactive and inactive sites, in the films formed from **1** and **4**. Cyclic voltammetry of organic redox solutes such as nitrobenzenes or benzoquinones at the electrodes coated with the ferrocene polymers from **1**–**3** indicated that these polymers can control the reversibility of the redox reactions of the solutes.

Introduction

Control of electrochemical reactions in solution by electroactive polymer coatings on electrode surfaces has received much recent attention because of the diversity of applications in electrochemistry, photoelectrochemistry, and electrochemical sensors and devices.[1] Preparation of the electrode films by electrochemical polymerization has afforded stable and pinhole-free films with a high concentration of electroactive sites. For metallocenes, vinylferrocene[2] and *N*-(*p*-ferrocenylphenyl)-β-(3-*N*-methylpyridyl)acrylamide hexafluorophosphate[3] have been studied as electrochemically polymerizable monomers.

We attempted to synthesize metallocene polymers in which metal is involved in the main chain by the electropolymerization method and have found that 1,1′-bis(chloromethyl)ferrocene (**1**) and 1,1′-bis(1-chloro-2-formylvinyl)cobaltocenium hexafluorophosphate (**4**) give electroactive polymer films by electrochemical reduction in acetonitrile.[4] These films carry charges for reduction of organic redox solutes in their reduced state and for oxidation of the solutes in their oxidized state.[4] These charge-transport properties have not been mentioned in previous reports on other metallocene electrode coatings notwithstanding that metallocenes have been extensively studied as electrode coatings.[5]

In this paper, we describe the detailed and extended study of the formation, characterization, and electrochemical properties of the electroactive films prepared by electroreduction of **1** and **4**, and new polymers of 1,1′-bis(1-chloro-2-formylvinyl)ferrocene (**2**) and (1-chloro-2-formylvinyl)ferrocene (**3**). The polymers of **1**–**4** are abbreviated PBCMF, PBCFVF, PCFVF, and PBCFVC, respectively. The purpose of this study is clarification of the preculiarity in nature of the polymers and finding a clue to comprehend their unusual one-way charge-transport properties. We have analyzed the volume concentration of ferrocene sites and electroactive sites in PBCMF and demonstrated the considerable difference between them. The role of electroinactive sites in the charge-transport process is mentioned.

Experimental Section

Materials. The ferrocene derivatives **1**,[6] **2**,[7] **3**,[7] and $Fe(C_5H_4Cl)_2$ (**5**)[8] were prepared by published methods. Other reagents were obtained from commercial sources and purified by sublimation, distillation, or recrystallization before use. A glassy-carbon rod, GC-30, and a plate of indium tin oxide (ITO) coated glass (30 $\Omega/\square$) used for the working electrode were supplied from Tokai Carbon Co. Ltd. and Nippon Sheet Glass Co. Ltd., respectively.

Preparation of $[Co(C_5H_4CCl{=}CHCHO)_2]PF_6$ (4). A cobaltocenium salt $[Co(C_5H_4COCH_3)_2]I_3$ was prepared by the reaction of $Co(C_5H_4COCH_3)_2$[9] (1.5 g) with I_2 (2.5 g) in THF (90 mL) for 14 h at room temperature under a nitrogen atmosphere, followed by the addition of hexane (300 mL); yield 1.8 g (50%). To a solution of $[Co(C_5H_4COCH_3)_2]I_3$ (1.0 g) in DMF (14 mL) was added slowly with stirring a mixture of $POCl_3$ (2.6 mL) and DMF (14 mL), and the solution was stirred for 15 min at 0 °C under nitrogen. After being stirred at room temperature for 18 h, the solution was concentrated at room temperature under vacuum. To the oily residue was added 40 mL of THF, and the mixture was stirred for 15 min. After filtration, the dark brown residue was dissolved in water and the insoluble part was filtered off. Addition of NH_4PF_6 (1.0 g) to the filtrate afforded a yellow precipitate **4**. It was recrystallized twice from acetone–diethyl ether; yield 0.21 g (27%). Anal. Calcd for $C_{16}H_{12}Cl_2CoF_6O_2P$: C, 37.60; H, 2.37; Cl, 13.87. Found: C, 37.42; H, 2.36; Cl, 13.45. ^1H NMR (in CD_3COCD_3): δ 10.22 (d, 2 H, J = 6 Hz, CHO), 7.07 (d, 2 H, $-CH{=}CCl$), 6.69 (m, 4 H, cyclopentadienyl), 6.34 (m, 4 H, cyclopentadienyl). IR (KBr disk): ν(C=O) 1685 cm^{-1}, ν(C=C) 1618 cm^{-1}.

Electrochemical Instrumentation and Procedures. Cyclic voltammetry was carried out with a Toho Technical Research Model 2000 potentiostat, 2230 function generator, and YEW 3086 X-Y recorder. All experiments were performed by using standard three-electrode cells equipped with a platinum-wire counter electrode and a Ag/Ag^+ (0.01 M $AgClO_4$ in acetonitrile) reference electrode calibrated to the Ag/AgCl electrode. The glassy-carbon rod (5.5-mm o.d.) was embedded in a Teflon bar, and the circular cross section was used as the working electrode. Its surface was polished with 0.3-μm alumina abrasive, cleaned by ultrasonic waves in redistilled water, washed with acetone, dried, and used for the electrochemical measurements. ITO glass electrodes (2 cm^2) were cleaned by ultrasonic waves in acetone, dried, and used for the measurements.

The ferrocene and cobaltocene polymer films were formed by electrochemical cycling through the reduction waves of the monomer or by potentiostating the working electrode at a potential sufficiently negative to reduce the monomer. Following the film deposition, the electrodes were rinsed with acetonitrile and stored in a drybox. The total amount

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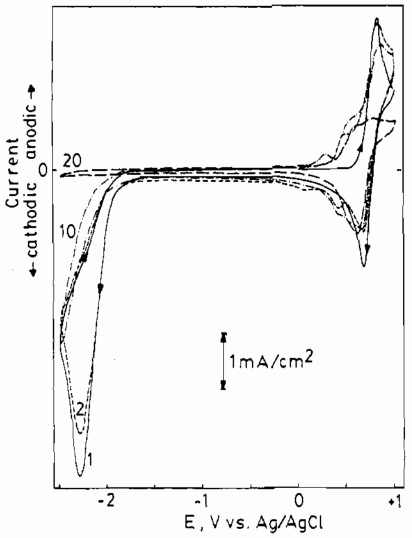

Figure 1. Reductive cyclic voltammetry of **1** (6 mM) at a GC electrode in 0.1 M Bu_4NClO_4/CH_3CN at 200 mV/s. Numbers in the figure refer to those of the cyclic scans.

of electroactive sites in the polymer, Γ (mol/cm^2), was determined by integration of the charge under the ferrocene/ferrocenium cyclic voltammetric wave in 0.1 M Bu_4NClO_4/CH_3CN or that of cobaltocene/cobaltocenium in 0.1 M Bu_4NI/CH_3CN.

Film Thickness Measurements. After a part of the formed film was sliced off with a cutter, film thickness was measured by an ELIONIX EMM-3000 scanning electron microscope with a PFM-1 profile measuring system and by a SLOAN DEKTAK-II surface profiler.

Spectroscopy. FT-IR and UV–visible spectra were monitored on a JEOL JIR-100 FT-IR spectrometer and a Shimadzu MPS-2000 UV spectrometer, respectively. SEM photographs were obtained under the condition of 20 kV of accelerating voltage and 5 μA of emission current with a JEOL FESEM-JFSM30 scanning electron microscope. Analysis of iron in the film was carried out with a Shimadzu EMX-SM X-ray microanalyzer.

Results and Discussion

Electrode Film Formation. Our expectation was that compound **1** could be reduced electrochemically to afford polymerizable radicals, $Fe(C_5H_4cH_2^\bullet)_2$, as represented in eq 1. This is because

$$Fe(C_5H_4CH_2Cl)_2 + 2e^- \rightarrow Fe(C_5H_4CH_2^\bullet) + 2Cl^- \qquad (1)$$

the cyclopentadienyl is estimated to show a reactivity similar to that of benzyl chloride. It has been known that α,α′-dihalogenoxylenes are polymerized by electroreduction in aprotic solvents.[10]

Cyclic voltammetry of **1** at a glassy-carbon (GC) electrode in 0.1 M Bu_4NClO_4/CH_3CN showed a redox reaction for the ferrocene/ferrocenium couple at +0.724 V vs. Ag/AgCl and an irreversible cathodic wave at ca. −2.2 V (see the first cycle in Figure 1). The electrochemical reaction at ca. −2.2 V is conjectured to be the halide reduction as represented in eq 1. Consecutive cyclic voltammetric scans between +1.0 and −2.5 V vs. Ag/AgCl in the solution of **1** formed electroactive films on the GC electrode surface (Figure 1). The PBCMF film formed by the potential scans showed a single symmetrical redox wave with the formal potential $E^{0\prime}$ = +0.525 V vs. Ag/AgCl in a clean 0.1 M Bu_4NClO_4/CH_3CN solution (Figure 2A). With slow scan rates (≤0.2 V/s) in 0.1 M Bu_4NClO_4/CH_3CN, the peak-to-peak separation, ΔE_p, remained constant at values of 30 mV and the peak currents varied linearly with the scan rate, as expected for the reaction of surface-localized material.[11] Surface coverage of electroactive sites, Γ, was calculated from the cylic voltammogram as described in the Experimental Section. It is noted that estimation of Γ by integration of charge under a potential step from 0 to +1.0 V vs. Ag/AgCl gave similar results.

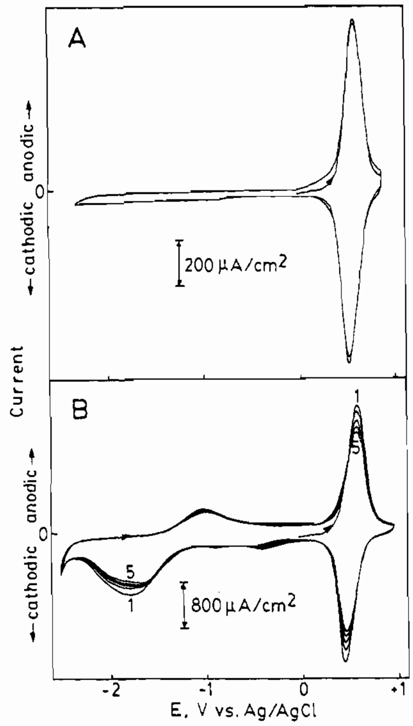

Figure 2. Cyclic voltammograms at 200 mV/s in 0.1 M Bu_4NClO_4/CH_3CN of a PBCMF-coated GC electrode formed from a 6 mM solution of **1**: (A) by consecutive potential scans between +1.0 and −2.5 V vs. Ag/AgCl for 20 cycles; (B) by constant-potential electrolysis at −2.5 V vs. Ag/AgCl for 24 min. $\Gamma = 8.0 \times 10^{-9}$ mol/cm^2 for A and 2.4×10^{-8} mol/cm^2 for B. Numbers in the figure refer to those of the cyclic scans.

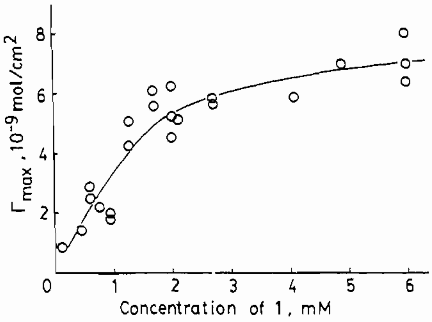

Figure 3. Relation of Γ_{max} to the concentration of **1** during electrolysis by consecutive potential scans between +1.0 and −2.5 V vs. Ag/AgCl in 0.1 M Bu_4NClO_4/CH_3CN.

The film was quite stable in air and in organic or aqueous solutions in the ferrocene state but decomposed slowly when electrochemically oxidized to the ferrocenium state. The decay kinetics of the ferrocenium on consecutive potential scans between 0 and +0.9 V vs. Ag/AgCl in 0.1 M Bu_4NClO_4/CH_3CN was second order, similar to that for the ferrocenes covalently linked to platinum electrodes reported by Lenhard and Murray.[12] The second-order decomposition rate constant for PBCMF was 9.3×10^5 cm^2/(mol s).

Film growth gradually became slow with increase in scan number and finally ceased due to the inhibition of reaction 1 by the formed film. The obtainable maximum surface coverage of electroactive sites, Γ_{max}, increased with the monomer concentration, but the degree of its dependence on the concentration became small at more than 2 mM as shown in Figure 3. The Γ_{max} value from a 6 mM solution was 8×10^{-9} mol/cm^2. The result shown in Figure 3 denotes that the film formed from a solution of lower monomer concentration inhibits reaction 1 more extensively than the one from a solution of higher concentration when Γ values of these films are similar. This is ascribable to lower permeability

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Table I. Electrochemical and Optical Properties of Metallocene Polymers[a]

polymer	$E^{\circ\prime}$, V vs. Ag/AgCl *b*	*c*	ΔE_p,[b,d] mV	$\Delta E_{1/2}$,[b,e] mV	Γ_{max}, mol/cm^2	*C*,[f] mol/cm^3	λ_{max},[f] nm
PBCMF/GC	+0.525		30	180	5×10^{-9}	3.8 (±0.4) × 10^{-4}	
PBCMF/ITO	+0.53 ± 0.01	+0.53	290 ± 90	230		3.8 (±0.5) × 10^{-4}	456 ± 7
PBCFVF/GC	+0.605		20	280	2×10^{-9}	1.3 (±0.1) × 10^{-4}	
PBCFVF/ITO	+0.64 ± 0.02	+0.61	120 ± 70	310			430 ± 2
PCFVF/GC	+0.528		40	260	1×10^{-8}	1.9 (±0.8) × 10^{-3}	
PCFVF/ITO	+0.54 ± 0.02	+0.53	170 ± 40	280			422 ± 14
PBCFVC/GC	−1.00	−1.00	70	240	6×10^{-8}	2.3 (±0.6) × 10^{-3}	
PBCFVC/ITO	−1.01 ± 0.02	−1.00	410 ± 220	350			410 ± 10

[a] PBCMF was formed by consecutive potential scans from a 2 mM solution of **1** and from 1 mM solutions of the corresponding monomers. [b] Obtained by cyclic voltammetry at the scan rate of 100 mM/s in 0.1 M Bu_4NClO_4/CH_3CN for PBCMF, PBCFVF, and PCFVF and in 0.1 M Bu_4NI/CH_3CN for PBCFVF. [c] Half-wave potential obtained by the Wrighton's method.[5a] [d] Peak-to-peak separation. [e] Half-height width of anodic peak. [f] Data for the ferrocene polymers in the reduced state and for PBCFVC in the oxidized state.

and/or lower volume concentration of electroactive sites in the film, C (which leads to a thicker film at a given Γ value), for the film formed from the solution with fewer monomers. We should note here that the Γ value estimated by cyclic voltammetry or potential step chronocoulometry does not exhibit the amount of all the ferrocene sites involved in PBCMF films (vide infra).

Constant-potential electrolysis of **1** at −2.5 V vs. Ag/AgCl also afforded electroactive films, where more than 2×10^{-8} mol/cm^2 of redox sites could be fixed from 6 mM solution of **1**. In the cyclic voltammogram of the film in clean 0.1 M Bu_4NClO_4/CH_3CN appeared broad cathodic and anodic waves at −1.8 and −1.0 V, respectively, besides the ferrocene/ferrocenium redox wave (Figure 2B). The waves were fairly reproducible in the repeated potential scans, as shown in Figure 1B, and it is not clear at this stage whether the waves were due to the C–Cl moieties remaining in the film or not.

The ferrocene derivatives **2** and **3** also afforded electroactive polymers PBCMF and PCFVF, respectively, on GC electrodes by consecutive potential scans, when the reduction of both the CHO and C–Cl moieties took place (Figure 4). The redox wave of the formed films appeared at ca. 0.5–0.6 V vs. Ag/AgCl in 0.1 M Bu_4NClO_4/CH_3CN. The difference in the number of ring substituents between **2** and **3** caused the slower but more continuous film growth and a larger number of electroactive sites fixed from the solution of **3** than of **2**.

Electroactive polymer films from a solution of cobaltocenium salt **4** were formed in 0.1 M Bu_4NI/CH_3CN. When consecutive potential scans between −0.1 and −1.5 V vs. Ag/AgCl at 100 mV/s were applied to a GC electrode in a 1 mM solution of **4**, the film growth continued during 50 scans and many more electroactive sites could be fixed than from the solution of **2**, the ferrocene derivative with the same substituents (Figure 5). This is because reduction of the C–Cl moiety in **4** at ca. −0.9 V can be mediated by the cobaltocenium sites in the formed film and consequently the film formation can be facilitated. The formal potential of the cobaltocene/cobaltocenium couple in the formed film was −1.00 V vs. Ag/AgCl in 0.1 M Bu_4NI/CH_3CN, more negative than that of monomer **4** by 0.8 V. In contrast to the ferrocene films, the cobaltocene electrode films, once dried, required several tens of scans to swell and to give a steady-state cyclic voltammogram of the film in a clean electrolyte solution.

Ferrocenes **1**–**3** and cobaltocenium salt **4** also afforded electroactive films on ITO electrodes in the same manner as described above. Some electrochemical properties of the four polymers are given in Table I. It should be noted that the peak-to-peak separations and the potential widths at peak half-height are quite larger for the films at ITO electrodes than at GC electrodes. These phenomena at ITO electrodes can be explained by high film resistance, repulsive site-to-site interactions within the film, and/or sluggish charge-transfer reactions at the electrode.[13] Because the electrode material gave a significant effect, the sluggish kinetics may be dominant. As GC has been known to have an active surface just after cleaning with polishing and washing,[14] the facile electron transfer at the GC/film interface is probably due to a strong interaction between the GC and the film such as C–C covalent bond formation by the reaction of the GC surface with

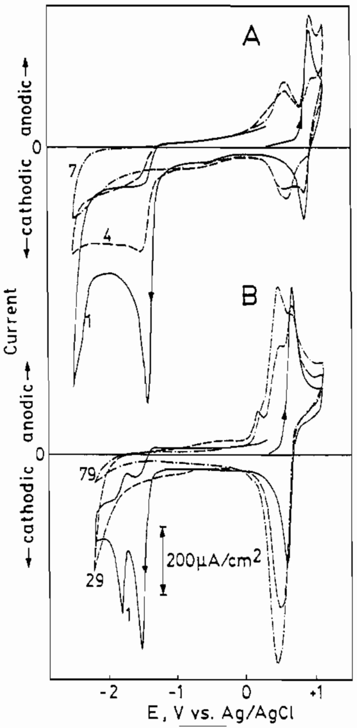

Figure 4. Reductive cyclic voltammetry of ferrocene derivatives **2** (A, 1 mM) and **3** (B, 1 mM) at a GC electrode in 0.1 M Bu_4NClO_4/CH_3CN at 100 mV/s. Numbers in the figure refer to those of the cyclic scans.

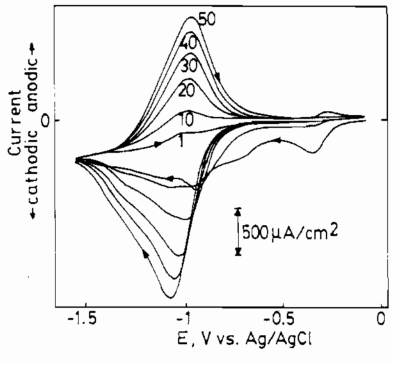

Figure 5. Reductive cyclic voltammetry of **4** (1 mM) at a GC electrode in 0.1 M Bu_4NI/CH_3CN at 100 mV/s. Numbers in the figure refer to those of the cyclic scans.

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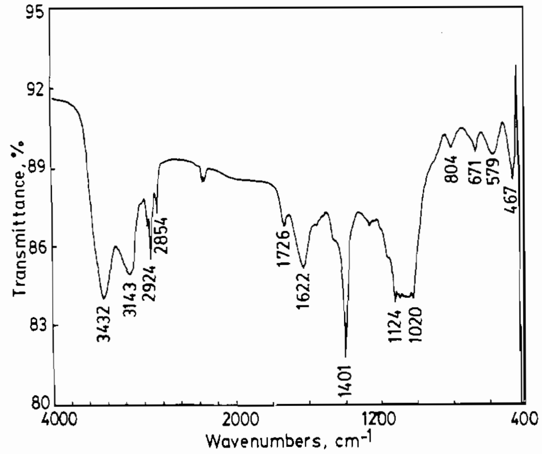

Figure 6. FT-IR spectrum of PBCMF formed from a 2 mM solution of **1** by consecutive potential scans.

the radicals formed by reaction 1. A method to measure accurate $E^{0\prime}$ values for sluggish electrode reactions has been demonstrated by Wrighton et al.[5a] A half-wave potential is determined for the plots of relative concentrations of the oxidized (or reduced) form in the film at given potentials. We measured $E^{0\prime}$ by this method for the films on ITO electrodes. The results, which are also given in Table I, are almost consistent with the values obtained from cyclic voltammograms.

Consecutive potential scans between +1.2 and −2.1 V vs. Ag/AgCl in a solution of **5** in 0.1 M Bu_4NClO_4/CH_3CN gave a polymer film on a GC electrode, but the film showed almost no redox reactions in a potential region between +1.0 and −2.0 V vs. Ag/AgCl in clean 0.1 M Bu_4NClO_4/CH_3CN.

Structure of the Polymer Films. The amount of iron in PBCMF films measured by an X-ray microanalyzer was proportional to Γ. Thickness of the films, PBCMF, PBCFVF, PCFVF, and PBCFVC, formed by consecutive potential scans from a 2 mM solution of **1** and from 1 mM solutions of **2**–**4**, respectively, was also proportional to Γ, indicating the constant distribution of the redox sites in the films. Volume concentrations of electroactive sites in the polymers, C, calculated from film thickness and Γ, are also listed in Table I. The C values for PBCMF and PBCFVF are quite small compared with that reported for poly(vinylferrocene).[15] This fact is discussed with reference to UV–visible spectroscopy in a later section.

The FT-IR spectrum of PBCMF is shown in Figure 6. Infrared absorptions at 2924 and 2854 cm^{-1} assignable to ν(CH) indicated the existence of the $-CH_2-$ moiety in the film. Characteristic bands of the ferrocene portion were observed at 3142 cm^{-1}, ν(CH), 1401 cm^{-1}, ν(CC), 1020–1120 cm^{-1}, ν(CC) and δ(CH), and 804 cm^{-1}, π(CH).[16] The spectrum indicates the structure $[(-CH_2C_5H_4)Fe(C_5H_4CH_2-)]_n$ formed by polymerization of the radical $Fe(C_5H_4CH_2^{\bullet})_2$ generated in reaction 1. The absorption of π(CH) at 804 cm^{-1} was considerably weak compared to that of the other bands. Similar weak absorptions for π(CH) were also observed in the spectra of the other polymers, PBCFVF, PCFVF, and PBCFVC. Hindrance of the π(CH) vibration of cyclopentadienyl ring may be caused by interaction with another ring of the adjacent metallocene site in the polymer. The structures of the linkage between metallocene sites in PBCFVF, PCFVF, and PBCFVC are rather complex. In their infrared spectra absorptions of ν(OH) and ν(CH) appeared at 3400 and 2850–2950 cm^{-1}, respectively, and those of ν(C=C) and ν(C=O) in the 1600–1700 cm^{-1} region were considerably weak. This implies that radicals formed by the reduction of CCl and C=CCHO groups were both involved in the polymerization reaction to give (3-hydroxypropyl)cyclopentadienyl structures linked to each other through an α-, β-, or γ-carbon. The protons consumed during the reduction of the aldehyde to alcohol may be provided by acetonitrile or a trace amount of impurity water.

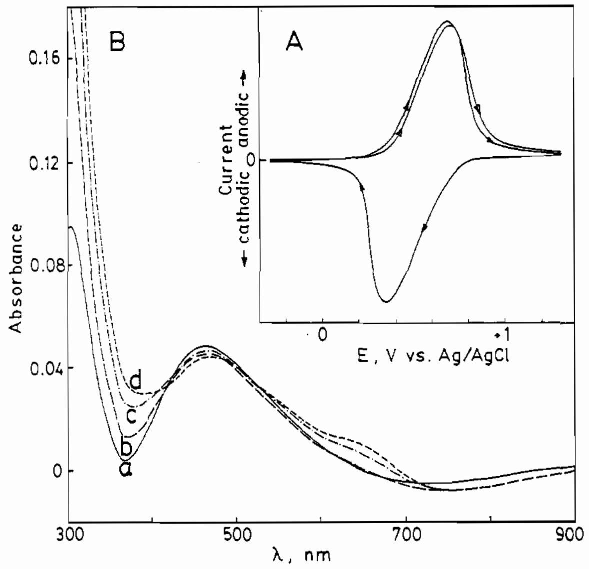

Figure 7. (A) Cyclic voltammogram for a PBCMF-coated ITO electrode with $\Gamma = 2.8 \times 10^{-8}$ mol/cm^2 at 100 mV/s in 0.1 M Bu_4NClO_4/CH_3CN. (B) UV–visible spectra of PBCMF at (a) −0.08, (b) +0.42, (c) +0.52, and (d) +0.82 V vs. Ag/AgCl in 0.1 M Bu_4NClO_4/CH_3CN.

The UV–visible absorption spectrum of PBCMF films formed on GC electrodes in a KBr disk showed an absorption at 260 nm due to a π–π^* transition of the cyclopentadienyl ring. The spectra of a PBCMF film on an ITO electrode formed by consecutive potential scans from 2 mM solution of **1**, at given potentials in 0.1 M Bu_4NClO_4/CH_3CN, are displayed in Figure 7B. At −0.08 V, when the PBCMF was in the reduced state, an absorption band at 449 nm due to the $^1A_{1g}$–$^1E_{1g}$ transition characteristic of a d^6 metallocene[17] was observed. The absorption of this transition also appeared for the other ferrocene and cobaltocenium films (see Table I). According to the positive shift of the potential, absorptions at 640 nm and at less than ca. 400 nm increased as shown in Figure 7. The difference of the spectra between +0.82 and −0.08 V apparently corresponded to the spectrum of the ferrocenium ion.[17] From the difference in absorbances at 640 nm and Γ was evaluated the absorption coefficient ϵ for several PBCMF films. The obtained ϵ was 470 ± 20, similar to the value for the $^2E_{2g}$–$^2E_{1u}$ transition of the ferrocenium ion.[17] It can be seen in Figure 7B that the band at 449 nm remained for the most part at +0.82 V when nearly all of the electroactive sites were oxidized. This indicates that all of the ferrocene sites were not necessarily electroactive under these conditions. The absorbance at 449 nm was proportional to Γ, and accordingly the film thickness. The volume concentration of ferrocene sites, C_{Fc}, in PBCMF was estimated provided that ϵ of the band was 100, as well as that of ferrocene.[17] The C_{Fc} value thus obtained was 7.5×10^{-3} mol/cm^3, which is reasonable in light of the size of ferrocene sites in the form of $[(-CH_2C_5H_4)Fe(C_5H_4CH_2-)]_n$. These results indicate that only $^1/_{20}$th of the ferrocene sites are electroactive in the film. This can be attributed to impossibility of counter ion (ClO_4^-) penetration into most of the film due to the closely packed structure. Evidence in support of this consideration was found in the observation that in the solution of a large anion, *p*-toluenesulfonate, the Γ value decreased to 82 ± 3% of that in the perchlorate solution. Change in the electroactivity of ferrocene electrode films by the size of electrolyte anions has previously been reported by Wrighton et al.[5a]

The C value of PBCMF films formed from a 6 mM solution of **1** was 5.5×10^{-4} mol/cm^3, estimated from Γ and film thickness;

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(15) The C values for poly(vinylferrocene) are estimated at ca. 6×10^{-3} mol/cm^3 from the data by: Umana, M.; Denisevich, P.; Rolison, D. R.; Nakahama, S.; Murray, R. W. *Anal. Chem.* **1981**, *53*, 1170.

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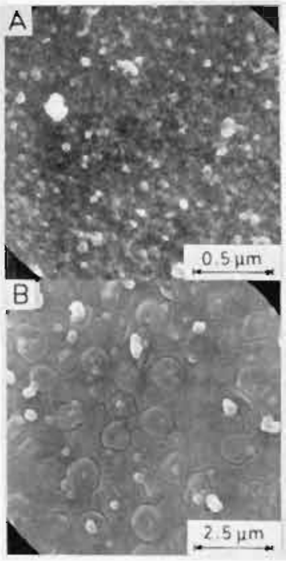

Figure 8. Scanning electron micrographs of (A) PBCMF on a GC electrode and (B) PBCFVC on an ITO electrode.

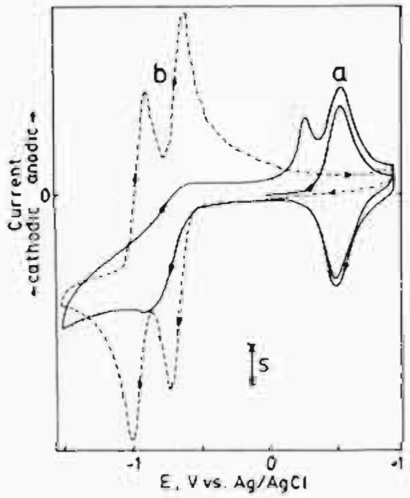

Figure 9. Cyclic voltammograms for a 2 mM solution of *o*-dinitrobenzene in 0.1 M Bu$_4$NClO$_4$/CH$_3$CN at 200 mV/s: (a) at a PBCMF-coated GC electrode; (b) at a bare GC electrode. S = (a) 125 and (b) 250 μA/cm^2.

this is larger than that for the films formed from a 2 mM solution of **1**. The ratio of C for those films, 1.4, corresponds to that of Γ_{max} displayed in Figure 3. Namely, the films with Γ_{max} from 2 and 6 mM solutions of **1** have similar film thcikensses. Thus, it can be concluded that the change of Γ_{max} by the monomer concentration as shown in Figure 3 is mainly attributed not to the difference in permeabilities of the films but to the difference in volume concentrations of electroactive sites in the film. The variety of C values in Table I suggests the differences in the ratio C/C_{Fc} or C/C_{Cc} (C_{Cc} is the volume concentration of cobaltocenium sites in the film)[18] for the four polymers.

Figure 8 shows scanning electron micrographs of PBCMF in the reduced state and of PBCFVC in the oxidized state. Spots of less than 0.1 μm and of ca. 0.8 μm in diameter with dented centers were observed in the surface of PBCMF and PBCFVC, respectively. It seems worthwhile to point out that some of the white solids of Bu$_4$NI adhere to the center of the spots, as shown in Figure 8B. If the counterion permeation occurs favorably at the spots, this heterogeneity must relate to the electroactivity of the metallocene sites in the film. Investigation of this relationship is being continued.

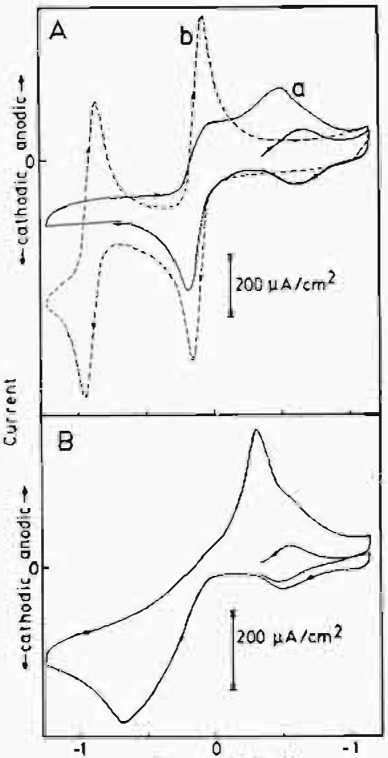

Figure 10. Cyclic voltammograms of DCBQ (A, 1.4 mM; B, 1.8 mM) in 0.1 M Bu$_4$NClO$_4$/CH$_3$CN at 100 mV/s: (Aa) at a PBCFVC-coated GC electrode; (Ab) at a bare GC electrode; (B) at a PCFVF-coated electrode.

Charge-Transport Properties of the Ferrocene Polymers. In Figure 9a is displayed a cyclic voltammogram of *o*-dinitrobenzene, a redox species whose formal potential is more negative than that of PBCMF, in 0.1 M Bu$_4$NClO$_4$/CH$_3$CN at a PBCMF-coated electrode. Only a single cathodic wave is shown around the formal potential of *o*-dinitrobenzene in the voltammogram at the coated electrode. A small anodic wave is observed at ca. +0.3 V vs. Ag/AgCl, the negative limit of PBCMF's oxidation wave. This indicates that the reoxidation of *o*-dinitrobenzene was mediated by the oxidation of electroactive ferrocene sites in PBCMF.[19] Similar voltammograms have been demonstrated in previous communications for 2,6-dichloro-*p*-benzoquinone (DCBQ) at a PBCMF-coated electrode[4a] and for ferrocene at a PBCFVC-coated one.[4b] In the latter case, the formal potential of ferrocene is more positive than that of PBCFVC, and an irreversible oxidation wave of ferrocene was shown around the formal potential of ferrocene.[4b]

We also examined the charge-transport properties of PBCFVF, PCFVF, and the electroinactive film formed from **5**. Cyclic voltaommograms of DCBQ at the polymer-coated electrodes are shown in Figures 10 and 11. In Figure 10, the irreversible charge-transport properties of PBCFVF and PCFVF, which are similar to those of PBCMF, are displayed, although some normal reoxidation wave of DCBQ ascribable to permeation of the solutes appeared at −0.1 V vs. Ag/AgCl in Figure 10A. In Figure 10B the cathodic peak due to the DCBQ reduction shifted to the negative potential, probably owing to a low conductivity of PBCFVF. At the electrode coated with electroinactive film prepared from **5**, a single cathodic wave of DCBQ reduction also appeared at −0.2 V vs. Ag/AgCl (Figure 11). Since the reoxidation wave of DCBQ at −0.1 V vs. Ag/AgCl seems small compared with the reduction wave, it is inferred that the irreversibility of the redox reaction of DCBQ also exists at this electrode.

The results described above show the generality of the one-way charge-transport properties for the ferrocene polymers formed by

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[18] The C_{Cc} value of PBCFVC evaluated from the size of the cobaltocenium site is ca. 5×10^{-3} mol/cm^3, and therefore C/C_{Cc} is ca. $^1/_3$.

[19] (a) Abrüna, H. D.; Denisevich, P.; Umaña, M.; Meyer, T. J.; Murray, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 1. (b) Denisevich, P.; Willman, K. W.; Murray, R. W. *Ibid.* **1981**, *103*, 4727.

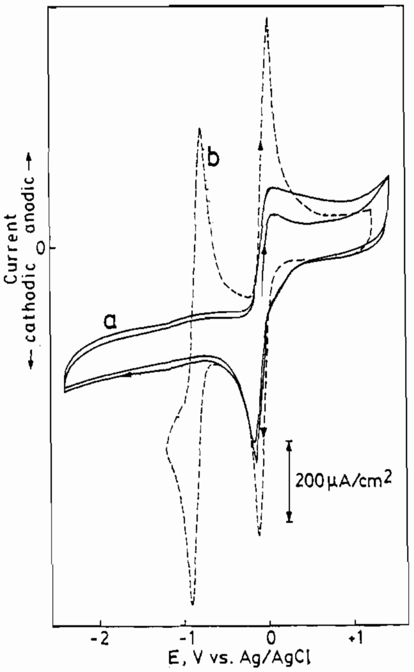

Figure 11. Cyclic voltammograms of DCBQ (1.7 mM) in 0.1 M Bu_4NClO_4/CH_3CN at 100 mV/s: (a) at a GC electrode coated with the polymer formed from 1 mM solution of **5** by consecutive potential scans between +1.2 and −2.1 V vs. Ag/AgCl for 40 cycles; (b) at a bare GC electrode.

the electrochemical polymerization in this study. The phenomena cannot be interpreted by simple permeation of the solutes within the film because of the irreversibility in the redox reaction of the solutes. They are also not explainable by the electron transfer mediated by redox reaction of electroactive sites in the polymers because of the thermodynamic disadvantage of charge transfer between the polymers and the solutes;[20] for example, the equilibrium constant K = ca. 10^{-13} for the electron transfer from ferrocenes to DCBQ. Therefore, a more complex mechanism is needed to interpret the results. One possible mechanism is based on the permeation of the solutes. The solute approaches the GC surface by diffusing through the polymer film and is then reduced directly. The anion thus formed is rapidly excluded from the neutral film and not reduced further. The anion at the film surface is oxidized via mediation by oxidation of electroactive sites in the film.

Another possible mechanism is based on the charge transfer at the film/solution interface. The redox solutes used in this study have been known to form charge-transfer complexes with ferrocenes.[21] Therefore, partial charge transfer can occur by the charge-transfer complex formation between the solutes and the ferrocene sites at the film surface. Holes thus generated on the film act as charge carriers through the film, and consequently reverse charge transport does not occur. Further reduction of the anionically charged solutes cannot proceed because of infeasibility of charge-transfer complexation with the ferrocene sites in the film. In this mechanism, electron transfer within the film must occur not only via electroactive sites but also via electroinactive ferrocene sites in order to explain the film electroactivity independence of cathodic peak currents for the solute reduction as shown in Figures 9–11.

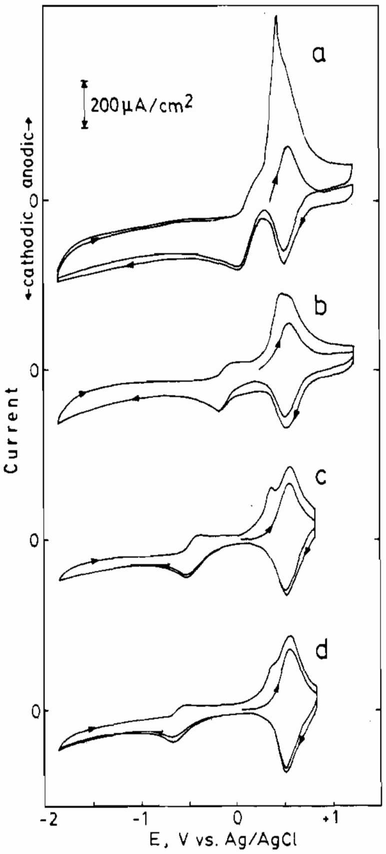

Figure 12. Cyclic voltammograms of benzoquinones at a PBCMF-coated GC electrode in 0.1 M Bu_4NClO_4 at 200 mV/s: (a) chloranil; (b) DCBQ; (c) *p*-benzoquinone; (d) α-naphthoquinone. Γ = 2.6, 2.1, 2.5, and 2.8 × 10^{-9} mol/cm^2 for a, b, c and d, respectively.

Figure 12 displays cyclic voltammograms of various *p*-benzoquinones at PBCMF-coated electrodes with similar Γ values. The cathodic peak currents for the reduction of solutes are in the order α-naphthoquinone < *p*-benzoquinone < DCBQ < chloranil. This order is consistent with that of reduction potential but not with that of molecular size. Therefore, the mechanism of charge transfer at the film/solution interface is more likely than the permeation mechanism. But this result is insufficient to warrant further discussion on the mechanism of the one-way charge-transport phenomena. One of the most determinative methods for distinction between the permeation and the charge-transfer reaction is rotating-disk voltammetry. A detailed mechanistic discussion using the data of this methodology will appear in future publications.

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Registry No. **1**, 32677-73-9; **2**, 1291-86-7; **3**, 1291-51-6; **4**, 104534-62-5; **5**, 1293-67-0; PBCMF homopolymer, 98702-20-6; PBCFVF, 36222-95-4; PCFVF, 36222-94-3; PBCFVC, 104469-76-3; PBCMF (SRU), 33660-04-7; $[Co(C_5H_4COCH_3)_2]I_3$, 104534-63-6; DCBQ, 697-91-6; C, 7440-44-0; SnO_2, 18282-10-5; In, 7440-74-6; $POCl_3$, 10025-87-3; Bu_4NClO_4, 1923-70-2; Bu_4NI, 311-28-4; *p*-benzoquinone, 106-51-4; α-naphthoquinone, 130-15-4; *o*-dinitrobenzene, 528-29-0; chloranil, 118-75-2.

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