Electrochemical Characterization of Redox Polymer Langmuir−Blodgett Films Containing Ferrocene Derivatives

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ABSTRACT: Redox properties of ferrocene derivatives incorporated into polymer Langmuir−Blodgett (LB) films have been investigated using cyclic voltammetry. The copolymers of *N*-dodecylacrylamide (DDA) with ferrocenylmethyl acrylate (FcA) and with vinylferrocene (vFc) were prepared as amphiphilic redox polymers. The spreading behavior of these copolymer monolayers on a water surface was investigated by measurement of the surface pressure−area isotherms. The isotherms show that the DDA/vFc copolymer monolayer is unstable, whereas the DDA/FcA copolymer forms a stable condensed monolayer on pure water when the mole fraction of FcA is less than ca. 54 mol %. Cyclic voltammograms for the DDA/FcA copolymer LB monolayer transferred on an ITO electrode exhibit a well-defined surface wave. The interfacial electron transfer process between the redox site incorporated to the polymer LB monolayer and the electrode surface is independent of the surface concentration of the redox site in the monolayer. On the other hand, the interlayer electron transfer process across layers in LB films depends on the surface concentration of the redox site.

Introduction

Redox polymer modified electrodes have received much attention from the viewpoint of understanding of fundamental electron transport processes and applications such as electrocatalysis, biosensor, and electrochemical devices.[1] The film thickness of redox polymers on the electrode surface can be varied in the wide range of submonolayer to several micrometers depending on techniques for preparations such as the casting method, spin coating method, chemical vapor deposition, and electropolymerization. These redox polymer films, however, usually do not have any ordered structure. Redox polymers with highly ordered molecular orientation on the electrode surface would be expected as key materials to control kinetics and directions of electron transfer events for new types of devices.

The Langmuir−Blodgett (LB) technique has an attractive feature to fabricate a molecular assembly with a controlled thickness at a molecular size and well-defined molecular orientation.[2] Recently, LB films consisting of some amphiphilic polymers[3] have been investigated to improve the poor thermal and mechanical stability of conventional LB films such as long alkyl chain fatty acids. Preformed *N*-dodecylacrylamide (DDA) polymer has been previously reported to have an excellent spreading behavior and to form stable LB films.[4] Furthermore, introduction of various functional groups such as aromatic chromophores[5−8] and chiral groups[9] into the polymer LB films as a comonomer of DDA has also succeeded.

Recently, the LB films[10−14] and self-assembled monolayers[15−22] with the ferrocene moiety have been well-studied about the interfacial electron transfer events between the ferrocene moiety and electrode surface because the ferrocene molecule has an electrochemically reversible property. Facci[10] and Majda[11−13] have studied the electrochemical behaviors of LB monolayers of (ferrocenylmethyl)dimethyloctadecylammonium hexafluorophosphate and *N*-octadecylferrocenecarboxamide, respectively. The electrochemical characterization of self-assembled monolayers of ferrocene-terminated alkanethiols on gold was carried out by Chidsey et al.[15,16] The bilayers of ferrocene LB monolayers and a self-assembled monolayer have been reported by Guo et al.[17−19] These redox amphiphiles described above are low molecular-weight compounds. Moreover, the study of electron transfer events at LB films and self-assembled monolayers is focused on the interfacial one between the electrode surface and the redox sites fixed on the electrode surface. In the present work, we introduce ferrocene derivatives into the polymer LB films to investigate electron transfer events at redox polymer LB films where the layered structure has been formed. We describe the spreading behavior of the monolayer of the DDA copolymer with ferrocene derivatives and the electrochemical properties of these redox polymer LB monolayers and multilayers. Since the polymer LB films have a layered structure, the electron transfer in the vertical direction (interlayer electron transfer) is clearly distinguished from that in the lateral direction (in-plane electron transfer). It is important to understand the interlayer electron transfer process as well as the interfacial one in order to fabricate intelligent molecular devices. The interlayer electron transfer events in redox polymer LB multilayers was described as a function of the number of deposited monolayers.

Experimental Section

Materials. *N*-Dodecylacrylamide (DDA) and ferrocenylmethyl acrylate (FcA) monomers were synthesized by the reaction of acryloyl chloride with dodecylamine and ferrocenemethanol, respectively, in the presence of triethylamine in dichloromethane at room temperature. The crude products were recrystallized from chloroform−hexane mixed solvent. Vinylferrocene (vFc) (Aldrich) was recrystallized from methanol before polymerization. DDA copolymers with vFc (DDA/vFc) and with FcA (DDA/FcA) were prepared by free radical polymerization in benzene at 60 °C with 2,2′-azobis(isobutyronitrile), as shown in Figure 1. The copolymers were purified twice by precipitation in a large excess of acetonitrile from chloroform solution and dried under vacuum at room temperature. The mole fractions of the ferrocene moiety in the copolymers were determined by the maximum absorbance of the ferrocene moiety using UV spectroscopy and are summarized in Table 1. Molar absorption coefficients of vFc and FcA homopolymers used as a standard compound for deter-

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Table 1. Monolayer, Electrochemical, and X-ray Diffraction Properties of DDA Copolymers with FcA

FcA mole fraction (*x*)	surface area[a] (nm^2/repeat unit)	collapse pressure (mN/m)	surface concn[b] (mol/cm^2)	layer-spacing (Å)
0	0.28	55		35.6
0.14	0.26	47		
0.20	0.25	44	6.87×10^{-11}	34.4
0.30	0.25	40	1.29×10^{-10}	35.6
0.41	0.25	30	1.99×10^{-10}	32.2
0.54	0.26	28	2.41×10^{-10}	32.6

[a] Limiting molecular occupied surface area (see text). [b] Surface concentration calculated by anodic current (see text).

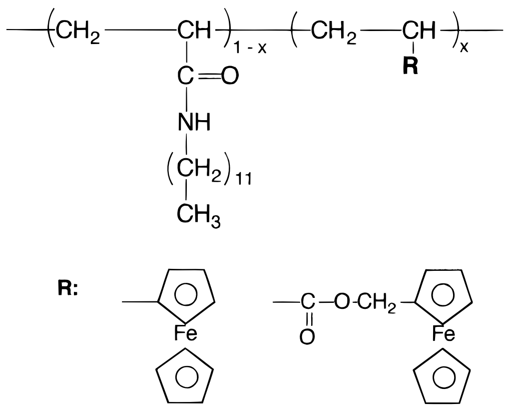

Figure 1. Structures of DDA copolymers with vFc and with FcA.

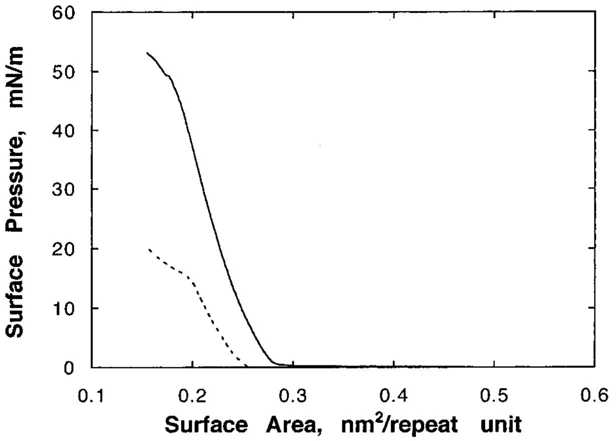

Figure 2. Surface pressure–area isotherms of DDA copolymers with vFc (dotted line) and with FcA (solid line) at 20 °C.

mination of copolymer composition were $\epsilon = 141\ \mathrm{M^{-1}\ cm^{-1}}$ at 437 nm and $110\ \mathrm{M^{-1}\ cm^{-1}}$ at 438 nm, respectively.

Instrumentation. The measurement of surface pressure–area isotherms and the deposition of the monolayers were carried out with a computer-controlled Langmuir trough (FSD-11, USI) at 20 °C. Distilled and deionized water (Millipore Milli-Q) was used for the subphase. Chloroform was used as a solvent for spreading the monolayer on a water surface. An ITO electrode and quartz substrate were employed as a substrate to deposit the monolayer. The ITO electrode was cleaned by sonication in a chemical detergent solution, water, acetone, and chloroform, successively. The quartz substrate was cleaned by immersion into a methanol solution of 5 wt % KOH, boiling in HNO_3 solution, and then washing with pure water. The monolayers of DDA/FcA copolymers were transferred onto these substrates at a dipping speed of 10 mm/min under a surface pressure of 20 mN/m at 20 °C. The monolayer is transferred onto the hydrophilic ITO electrode from the water surface.

Cyclic voltammetry was performed using a potentiostat (HA-501, Hokuto) and a function generator (HB-104, Hokuto). Current–potential curves are recorded on an *x*–*y* recorder (Graphtec WX1000). The electrochemical cell is equipped with a window for mounting the ITO electrode. The ITO electrode is mounted at the cell window using a silicon rubber O-ring (14 mm o.d.). The electrode area of 1.54 cm^2 is exposed to the electrolyte solutions. A Pt wire is used as an auxiliary electrode and the potential is referenced to a saturated calomel electrode (SCE). A $NaClO_4$ solution (1.0 M) is employed as an electrolyte solution.

Low-angle X-ray diffraction patterns were measured using an X-ray diffractometer (Rigakudenki RAD-C). The DDA/FcA copolymer LB film with 40 layers was used for low-angle X-ray diffraction measurements.

Results and Discussion

Polymer Monolayer at the Air–Water Interface. Figure 2 shows the surface pressure–surface area isotherms of the monolayers of DDA/vFc and DDA/FcA copolymers with 0.30 mole fraction of ferrocene moiety. Apparently, the monolayer properties varied largely with the comonomer of ferrocene derivatives. The isotherm of the DDA/vFc copolymer monolayer shows a low collapse pressure (15 mN/m). In contrast, the isotherm of the DDA/FcA copolymer monolayer shows a steep increase in surface pressure with a higher collapse pressure (40 mN/m). It indicates that the DDA/vFc copolymer forms an expanded form, while the DDA/FcA copolymer forms a stable condensed monolayer. The difference in the monolayer properties on the water surface between vFc and FcA can be explained by two factors: One is the balance of the hydrophobic–hydrophilic interaction of the DDA copolymer formed. The other is freedom in rotation of the ferrocene moiety around the polymer chain. As FcA has an amphiphilic character consisting of a hydrophobic ferrocene moiety and a relatively hydrophilic acryloyl group, the DDA copolymers with FcA can hold the same amphiphilicity as the DDA homopolymer. Meanwhile, the DDA/vFc copolymer becomes more hydrophobic than the DDA homopolymer. The ferrocene moiety of vFc is directly attached to the polymer chain, while that of FcA is linked to the polymer chain through an acryloyl group which acts as a spacer. The latter does not interfere with polymer assembly for stable monolayer formations. In the subsequent experiments, the DDA/FcA copolymers are employed.

The surface pressure–area isotherms of DDA copolymers with various mole fractions of FcA are illustrated in Figure 3. As the mole fraction of FcA increases from 0.14 to 0.54, the collapse pressure decreases gradually from 55 to 28 mN/m. It is of interest that the monolayer of the copolymer with even 0.54 mole fraction of FcA gives a well-defined π–A isotherm with a steep rise in surface pressures and a high collapse pressure. We have never observed such a stable monolayer having a high collapse pressure among the DDA copolymers containing such a high content of functional groups in the previous works. The limiting molecular occupied surface area of the DDA/FcA copolymer, which is obtained by the extrapolation of the linear part of the π–A curve to zero surface pressure, is almost constant

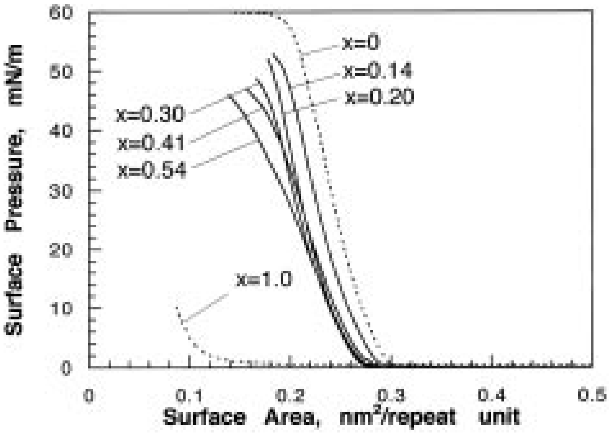

Figure 3. Surface pressure−area isotherms of DDA copolymers with various mole fractions of FcA at 20 °C.

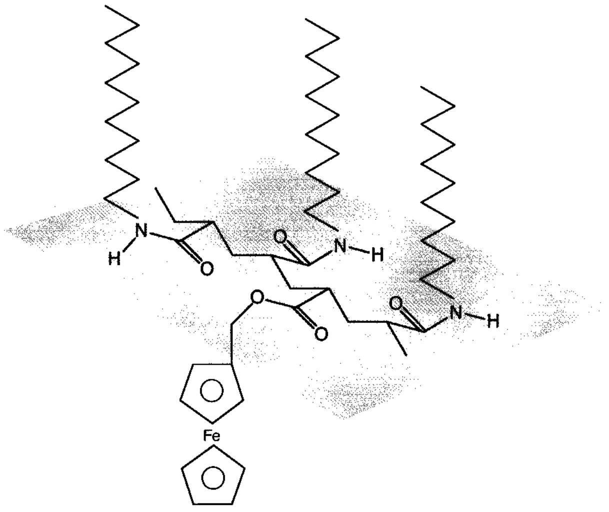

Figure 4. Schematic representation of the three-dimensional structure of a monolayer of DDA/FcA copolymer on the water.

irrespective of mole fraction of FcA. Assuming that the limiting area of the DDA homopolymer[3] is 0.28 nm^2/repeating unit, the limiting area of the FcA moiety in the copolymers is calculated to be 0.13−0.24 nm^2/repeating unit.[20] This means that the ferrocene moiety occupies no surface area on the air−water interface. The molecular occupied limiting areas of *N*-octadecylferrocenecarboxamide[12] and (ferrocenylmethyl)dimethyloctadecylammonium hexafluorophosphate[10] are reported to be 0.48 ± 0.02 and 0.51 nm^2/molecule, respectively. We suppose that the ferrocene moiety of the DDA/FcA copolymer squeezes out into the water phase.[21] We propose the orientation of the DDA/FcA copolymer monolayer on the water surface as illustrated in Figure 4. These DDA/FcA copolymer monolayers can be safely transferred onto ITO electrodes as a Y-type film with a transfer ratio of unity.

Electrochemical Behavior of the Polymer LB Films. Figure 5 shows cyclic voltammograms for DDA copolymer LB monolayers with various FcA contents at 50 mV/s scan rate. All voltammograms show a well-defined surface wave consisting of symmetric oxidation and reduction peaks of the ferrocene moiety. The potential differences of full width at half-maximum (ΔE_{fwhm}) are 130−170 mV, which are larger than the theoretical value, 90 mV.[22] This difference implies that the ferrocene moiety exists in a different molecular environment in the LB monolayer. However, the ferrocene moiety with a hydrophilic acryloyl group would be not buried into the hydrophobic alkyl chains of the monolayer because the well-defined electrochemical response as a whole is observed. In the cyclic voltammograms of a self-assembled monolayer of alkanethiols with ferrocene derivatives, Chidsey et al.[15,16] have reported that the ferrocene moiety with a polar ester group shows thermodynamically ideal surface electrochemistry whereas the nonpolar ferrocene moiety gives a broadened electrochemical feature. Finklea et al.[23,24] have also pointed out that the ideal behavior in the cyclic voltammograms of pentaammine(pyridine)ruthenium is attributed to the hydrophilic nature of the redox center. In fact, the cyclic voltammogram of the DDA/vFc monolayer LB film on the ITO electrode shows a broadened surface wave voltammogram because of the hydrophobicity of vFc. Therefore, it is important for redox species connected to alkyl chains to have a hydrophilic nature for the electrochemical reversibility. Surface concentrations of the ferrocene moiety of the DDA/FcA copolymer monolayer LB films which are calculated by integrating the anodic current in the cyclic voltammogram are summarized in Table 1. The surface concentration can be varied from 6.87 × 10^{-11} to 2.41 × 10^{-10} mol/cm^2 by changing the mole fraction of FcA in the DDA copolymers. Assuming that the surface area of the ferrocene moiety is 0.50 nm^2/molecule, the highest surface concentration of the ferrocene moiety is estimated to be 3.32 × 10^{-10} mol/cm^2 at the monolayer of the FcA homopolymer. Thus, these values of the surface concentration are reasonable at DDA/FcA monolayer LB films.

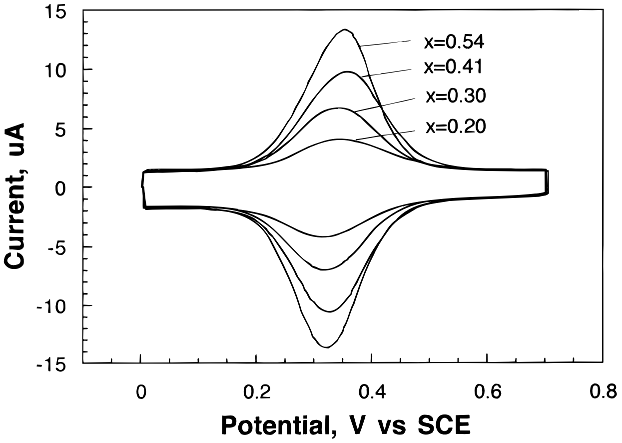

Figure 5. Cyclic voltammograms for DDA copolymers with various mole fractions of FcA LB monolayer on ITO electrodes at the scan rate 50 mV/s.

The shapes of the cyclic voltammograms are independent of the scan rate in the range of 1−500 mV/s, and also the height of current peaks increases linearly with the scan rate irrespective of the surface concentration of DDA/FcA monolayer LB films (Figure 6). These results suggest that the rate of interfacial electron transfer reaction between the ferrocene moiety incorporated into polymer LB films and the electrode surface is fast enough at scan rates less than 0.5 V/s. They also indicate that the kinetics of the interfacial electron transfer process is independent of the surface concentration of the ferrocene moiety in the LB monolayer. Consequently, the ferrocene moiety, one of the redox active species, could be incorporated into highly ordered LB films with the copolymerization of DDA which has an excellent property of monolayer formation. The ferrocene moiety with the hydrophilic group in the LB

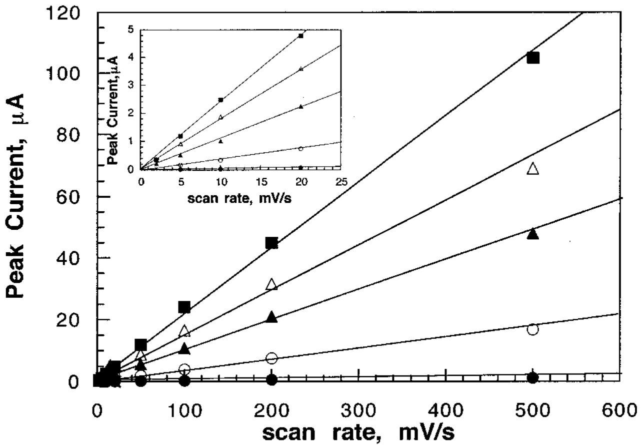

Figure 6. Plots of anodic peak current vs scan rate of the DDA copolymers with various mole fractions of FcA LB monolayer on the ITO electrode: $x = 0.54$, closed square; $x = 0.41$, open triangle; $x = 0.30$, closed triangle; $x = 0.20$, open circle; $x = 0.14$, closed circle.

film behaves as the electrochemically reversible compound.

As LB multilayers have a well-defined layer structure, electron transfer processes in LB multilayers should be distinguished between in-plane (lateral process) and interlayer (vertical process). We have measured cyclic voltammograms as a function of the number of deposited layers to discuss the interlayer electron transfer process. Figure 7 indicates cyclic voltammograms for the LB films with 0.41 mole fraction of FcA at various scan rates. The voltammogram is symmetric for the monolayer LB film, as mentioned above. As the number of LB monolayers increases (three and five layers), the voltammograms become distorted, because the rate of interlayer electron transfer becomes slower with increasing distance between the redox site and the electrode surface. However, voltammograms still show a surface wave shape and the charge obtained by integrating the anodic current in the voltammogram is constant at low scan rates. It suggests that all redox species in the LB multilayer films (three and five layers) are electroactive and the interlayer electron transfer process across the layers of LB multilayer films occurs by the electron hopping mechanism. On the other hand, Figure 8 shows cyclic voltammograms for the LB films with 0.20 mole fraction of FcA as a function of scan rates. The voltammograms of the LB monolayer with 0.20 mole fraction of FcA is symmetric as well as that with 0.41 mole fraction of FcA. However, those of LB multilayer films indicate no surface wave shapes and the diffusional tails appear. Peak currents show no increase with the number of layers of LB film. The rate of the interlayer electron transfer becomes inefficient when the surface concentration of the ferrocene moiety in the LB monolayers decreases. Logarithmic plots of anodic peak current vs scan rate are shown in Figure 9. The slopes for the DDA copolymer with 0.41 mole fraction of FcA are unity for the monolayer and three and five layer LB films. In contrast, in the case of lower surface concentration, 0.20 mole fraction of FcA, the slope is unity for the monolayer LB film, while they are smaller than unity for the three and five layer LB films. In addition, the current observed for the three and five layers of DDA copolymer with 0.20 mole fraction of FcA is not different from that for the monolayer in the region of high scan rates, as shown in Figure 9. These imply that only the first layer of LB multilayer films is electroactive and the other layers of LB multilayer films cannot be oxidized or reduced in the region of these high scan rates at the low surface concentration of ferrocene moiety in the LB films. Therefore, the interfacial rate of electron transfer between the ferrocene moiety in the first layer of the LB multilayers and electrode interface is fast enough to observe current response. On the other hand, the rate of interlayer electron transfer across the layers of the LB multilayers depends on the surface concentration in the layer of LB films. As the rate of electron transfer is known to depend on the distance between redox species, the layer spacing in the LB multilayer films was measured by low-angle X-ray diffraction. Figure 10 shows X-ray diffraction patterns for the LB multilayers with 0.41 and 0.20 mole fraction of FcA. One Bragg peak appears in both X-ray diffraction patterns. The layer spacing was calculated to be 3.22 and 3.44 nm at 0.41 and 0.20 mole fraction of FcA, respectively (Table 1). The spacing tends to decrease with increasing mole fraction of FcA in the polymer LB film. As space-filling molecular models of DDA indicate that the maximum length of dodecyl alkyl chains is estimated to be 1.8 nm, a tilt of the dodecyl alkyl chain in the present LB films is proposed. A decrease in the spacing with increasing mole fraction of FcA seems to correspond to a change of tilt angle. Therefore, at the high surface concentration of redox species, all layers of multilayer LB films are electroactive because the distance of electron transfer between layers is shorter than that at the low surface concentration.

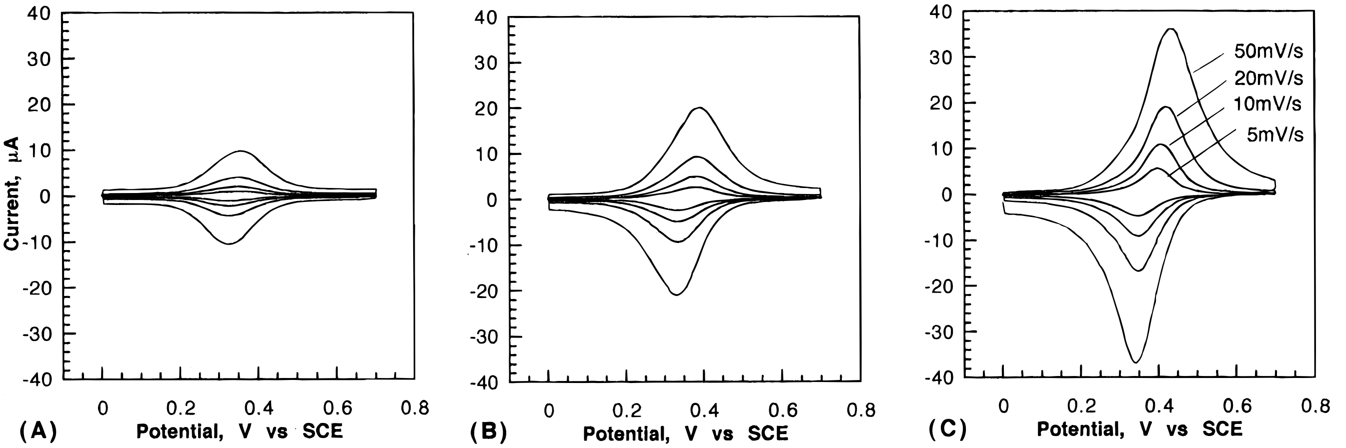

Figure 7. Cyclic voltammograms for the DDA copolymer with 0.41 mole fraction of FcA LB monolayer and multilayers on the ITO electrode with various scan rates: monolayer (A); three layers (B); five layers (C).

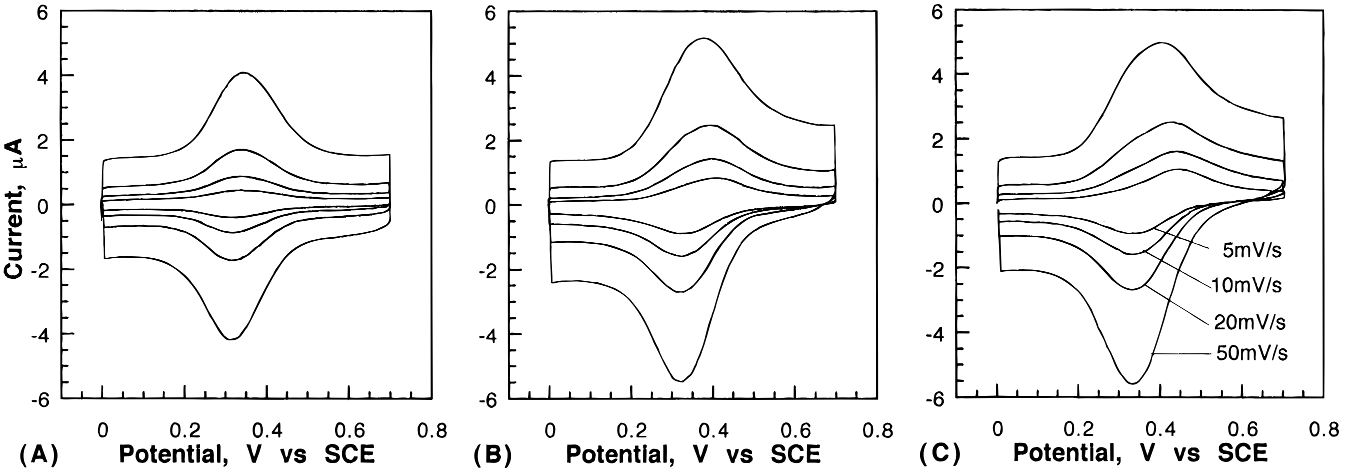

Figure 8. Cyclic voltammograms for the DDA copolymer with 0.20 mole fraction of FcA LB monolayer and multilayers on the ITO electrode with various scan rates: monolayer (A); three layers (B); five layers (C).

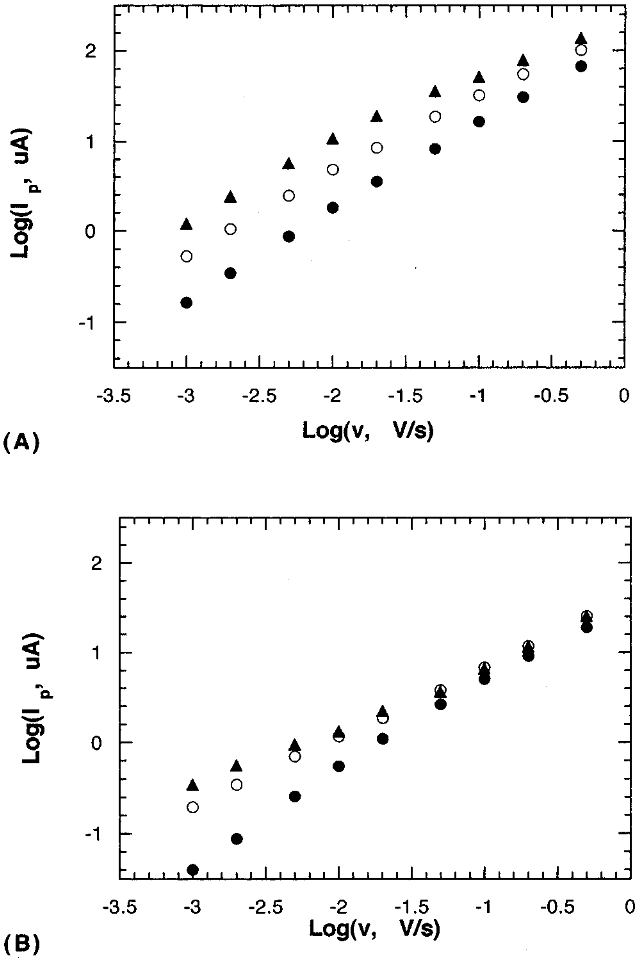

Figure 9. Logarithmic plots of anodic peak current vs scan rate of the DDA copolymer with various mole fractions of FcA LB monolayer and multilayers on the ITO electrode: monolayer, closed circles; three layers, open circle; five layers, closed triangle.

Conclusively, the ferrocene moiety, one of the redox species, can be incorporated into polymer LB films. The DDA/FcA copolymer forms a stable monolayer on the water surface. The polymer monolayer is transferred onto a solid support with a transfer ratio of unity, giving Y-type LB films. The rate of interfacial electron transfer process between the ferrocene moiety and the electrode surface is fast enough and is independent of the surface concentration of the ferrocene moiety in the DDA

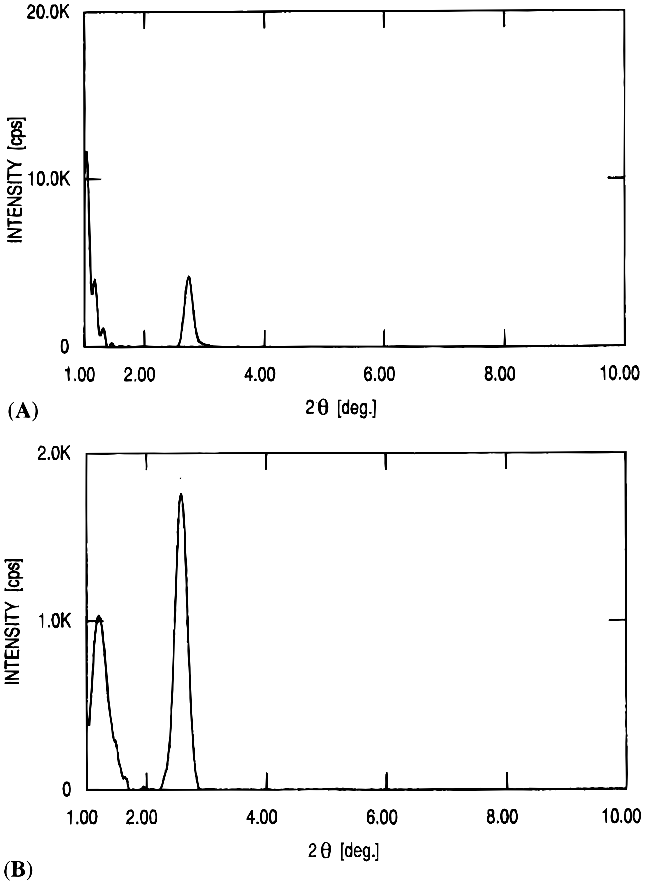

Figure 10. Low-angle X-ray diffraction patterns of DDA/FcA copolymer LB multilayers on quartz. The mole fractions of FcA are 0.41 (A) and 0.20 (B).

copolymer LB film. On the other hand, the rate of the interlayer electron transfer process across layers of LB multilayers depends on the surface concentration of the ferrocene moiety. On the basis of these results, further studies fabricating the hetero redox polymer LB films are in progress.

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(20) The limiting areas for FcA (A_{FcA}) in the copolymer were calculated using the limiting areas for the copolymer ($A_{\mathrm{copolymer}}$) and DDA homopolymer (A_{DDA}) and also using the mole fractions of DDA (x_{DDA}) and FcA (x_{FcA}) in the copolymers under the assumption of the additivity of molecules according to the below equations.

$$A_{\mathrm{copolymer}} = A_{\mathrm{DDA}}x_{\mathrm{DDA}} + A_{\mathrm{FcA}}x_{\mathrm{FcA}}$$

$$1 = x_{\mathrm{DDA}} + x_{\mathrm{FcA}}$$

(21) Copolymerization reactivity ratios of FcA and DDA calculated using $Q-e$ values are 0.39 and 2.33, respectively. The FcA monomer is alternatively polymerized.

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