Electrochemical Behavior of Hetero-Deposited Redox Polymer Langmuir-Blodgett Films with Ferrocene and Tris(bipyridine)ruthenium Derivatives

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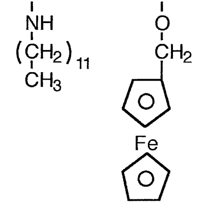
Stable redox polymer monolayer and Langmuir-Blodgett (LB) films can be prepared from amphiphilic copolymers of *N*-dodecylacrylamide (DDA) with ferrocene derivative (Fc) and with ruthenium complex (Ru). Electrochemical properties of the LB films fabricated from the hetero-deposition of Ru and Fc copolymer monolayers onto ITO electrodes were investigated using cyclic voltammetry. The results demonstrate that the hetero-deposited redox polymer LB films show rectifying property and charge storage.

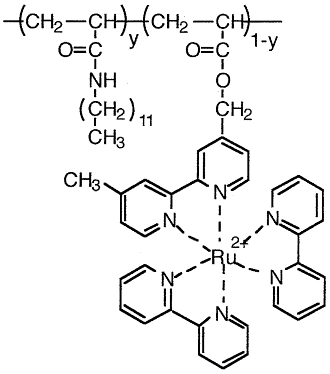
LB technique is one of methods to fabricate molecularly highly ordered structures and ultrathin films. In particular, hetero-deposited LB films are of great interest for the application to artificial photosynthesis[1,2] and electrochemical molecular devices.[3] The hetero-deposited LB films have been expected to develop novel functions compared with homogeneous LB films, because various spatial arrangements of different functional molecules depending on the purpose are possible. Recently, the unique electrochemical property of the polymer assembly prepared from two different redox polymers has first been reported by Murray et al.[4] The redox polymer films have become possible to develop a rectifying function using the redox potential difference between redox species. However, in the polymer films prepared by the electropolymerization, it is difficult to control the orientation and the distance of redox species and to form ordered molecular arrangement. In this work, we tried to fabricate hetero-deposited LB films by deposition of two different monolayers of redox polymers.

An attempt to incorporate various redox species into polymer LB films has been carried out. Polymer LB films have the advantage of their superior thermal and mechanical stability in comparison with low molecular weight LB films such as long alkyl chain fatty acid. We have found that DDA polymer has an excellent ability to form a stable monolayer and LB film.[5] Furthermore, polymer LB films of DDA whose alkyl chain consists of 12 carbon atom can reduce alkyl chain length. In general, low molecular weight redox amphiphiles are stearyl derivatives. This short alkyl chain length makes facilitate the electron transfer reaction across the interlayer of LB films. In this report, we have prepared the hetero-deposited LB film using DDA copolymers with Ru and with Fc. The electrochemical behavior of the LB films deposited on ITO electrodes has been described.

The Fc copolymer was prepared as described elsewhere.[6] The Ru copolymer was prepared as follows; 4-hydroxymethyl-4'-methyl-2,2'-bipyridine was synthesized from 4,4'-dimethyl-2,2'-bipyridine according to Meyer et al.[7] The resulting compound was reacted with acryloyl chloride in the presence of triethylamine in chloroform at room temperature to obtain 4-(acryloylmethyl)-4'-methyl-2,2'-bipyridine as a ligand monomer. The copolymer of DDA with the ligand monomer was prepared by free radical polymerization in benzene. The resulting copolymer was refluxed with *cis*-bis(2,2'-bipyridine)dichlororuthenium(II) in ethanol. The copolymer complexed with Ru was purified twice by precipitation in a large excess of diethyl ether from ethanol solution. The mole fractions of the redox species in the copolymers were determined to be 0.54 and 0.11 for Fc and Ru copolymers, respectively by UV-vis absorption measurement.



Fc Copolymer



Ru Copolymer

Chloroform solutions of the copolymers were spread on the water surface in Langmuir trough (FSD-110, USI) to measure surface pressure (π) - area (A) isotherms of monolayers (Figure 1). The π-A isotherms show the formation of a stable condensed monolayer with a high collapse pressure as same as that of DDA homopolymer.[5] The limiting area of Fc, Ru copolymer and DDA homopolymer were 0.26, 0.25 and 0.28 nm^2 repeat unit^{-1}, respectively. The limiting area of ferrocene and ruthenium moiety in the copolymers are calculated to be 0.24 and 0.01 nm^2 molecule^{-1}. The cross-sectional area of ferrocene[8] and ruthenium tris(bipyridine) derivatives[9] are reported to be ca. 0.50 and 1.0 nm^2 molecule^{-1}, respectively. Therefore, it is supported that ferrocene and ruthenium complex moiety would exist in the water subphase. The monolayers of Fc and Ru copolymers could be

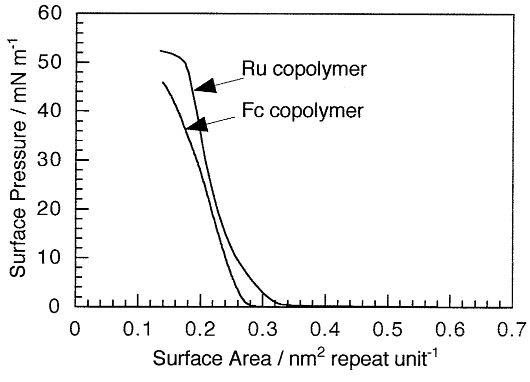


Figure 1. Surface pressure-area isotherms of Fc and Ru copolymers at 20 °C.

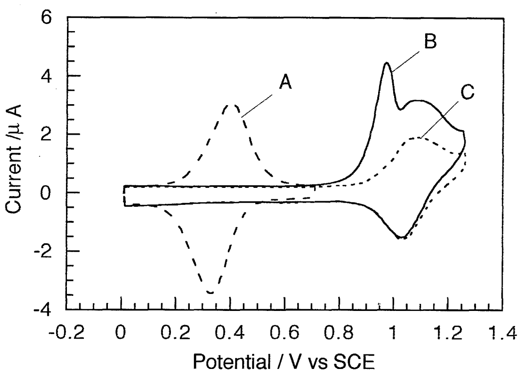


Figure 2. Cyclic voltammograms for redox polymer LB films on ITO electrodes at 10 mV sec^{-1} scan rate in 1.0 M $NaClO_4$ solution. (A) homogeneous Fc LB films with 3 layers on the ITO electrode, (B) hetero-deposited LB films transferring Ru copolymer with 3 layers and Fc copolymer with 2 layers on the ITO electrode successively at the first scan, (C) the same electrode with (B) at the second scan.

transferred onto ITO electrode at a dipping speed of 10 mm min^{-1} under a surface pressure of 20 mN m^{-1} at 20 °C as Y-type film with a transfer ratio of unity.

Cyclic voltammograms for the hetero-deposited redox polymer LB film and Fc LB film were measured using a potentiostat (HA-501, Hokuto) and a function generator (HB-104, Hokuto) (Figure 2). The hetero-deposited LB film with three Ru monolayers and two Fc monolayers are deposited on the ITO electrode as illustrated in Figure 3. The voltammogram of the Fc LB film was a symmetric shape at 0.34 V vs SCE, indicating a typical surface wave (Figure 2A). In the hetero-deposited LB films, no oxidation current of Fc was observed at about 0.34 V vs SCE. Outer Fc LB film are not oxidized in the region of the oxidizing potential of Fc species at the first scan. Because inner Ru LB films behaves as an insulator for the outer Fc LB films (a, Figure 3). A catalytic sharp current appeared at the potential around 0.8 V vs SCE, where Ru^{2+} is oxidized (Figure 2B). At this potential, ferrocene sites are catalytically oxidized through Ru^{3+} sites in the inner LB film at the Ru/Fc interface (b, Figure 3). On the other hand, a reduction current peak of Ru^{3+} sites is only observed at the reverse potential scan. Because Ru^{2+} sites in the inner LB film is thermodynamically incapable of mediating the reduction of the outer oxidized Fc LB film (d, Figure 3). Furthermore, no reduction wave for the outer Fc LB film is observed because of the insulation of the inner Ru LB film (c, Figure 3). The outer LB film sites remain trapped in the oxidized Fc state, which is regarded as a charge storage. Consequently, the voltammogram at the second scan is the same with that of Ru LB films as shown in Figure 2C. These results demonstrate that the unidirectional electron transfer across the interface between Ru and Fc LB films is realized by the hetero-deposited redox polymer LB films. As ruthenium complex is well-known as a photosensitizer, the photoelectrochemical study of this hetero-deposited redox polymer LB films system is now in progress.

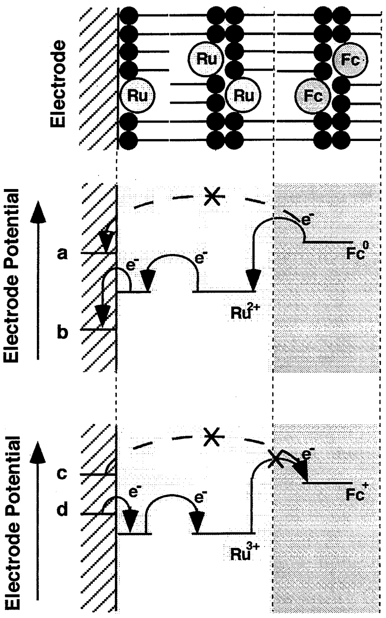


Figure 3. Schematic representation for the hetero deposited LB film structure on the ITO electrode and the mechanism of the electron transfer reaction between Fc and Ru LB films.

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References and Notes

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