

PREPARATION OF PHOTOFUNCTIONAL POLYMER THIN FILMS BY LANGMUIR-BLODGETT TECHNIQUE

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Abstract Polymer LB films containing photofunctional groups were prepared by the copolymerization of N-dodecylacrylamide (DDA), which has an excellent property to form a stable monolayer and LB multilayers with photofunctional monomers. *Tris*(2, 2'-bipyridine) ruthenium complex, $\text{Ru}(\text{bpy})_3^{2+}$, one of the most well-known redox-active sensitizer, was incorporated into the DDA copolymer. The photogalvanic effect based on the photoinduced electron transfer using the ruthenium complex in the polymer LB monolayer was discussed.

Keywords Photofunctional polymer, Polymer LB film, N-Dodecylacrylamide, Ruthenium complex

INTRODUCTION

Langmuir-Blodgett (LB) method is one of the most useful techniques for the fabrication of functional organic ultrathin films^[1]. We have attempted to prepare functional polymer ultrathin films by the Langmuir-Blodgett technique. Recently, N-dodecylacrylamide polymer (PDDA) was found to form a stable condensed monolayer and give a highly ordered polymer LB film^[2]. Moreover, we have proposed a copolymerization method to incorporate various functional groups into the polymer LB films with the help of the excellent properties of PDDA^[3-6]. In this paper the monolayer formation from the copolymers containing ruthenium complex as a photofunctional group (Fig.1) was described.

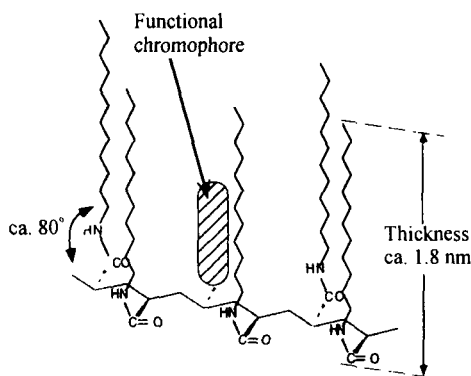
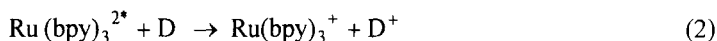
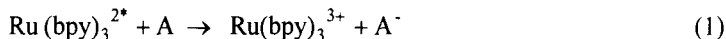


Fig.1 Molecular orientation of the acrylamide copolymer monolayer containing functional group

Photoinduced electron transfer reactions play an important role in many areas of application,

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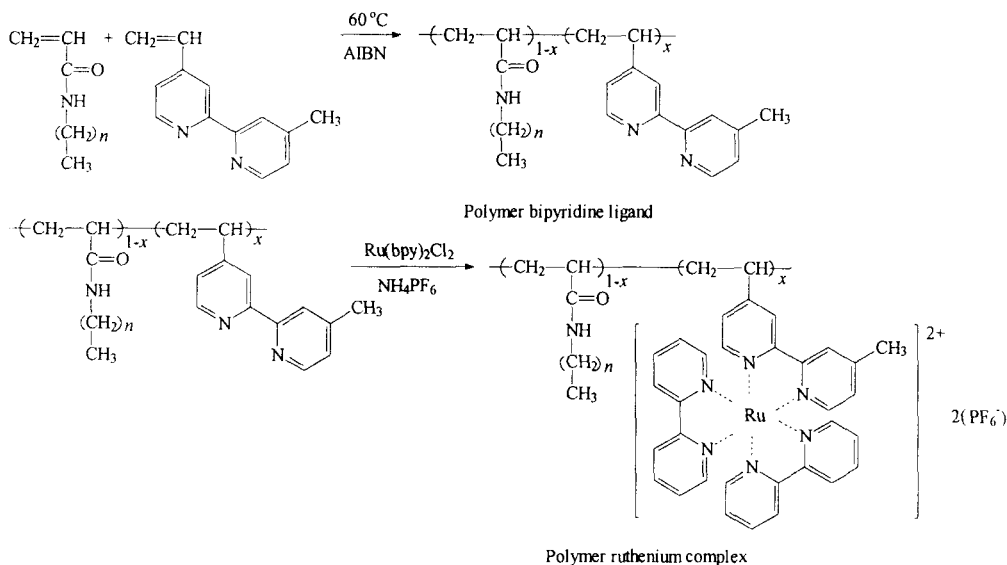
especially in photofunctional devices^[7]. It is known that photoredox processes are based on photoinduced electron transfer reaction and the efficiency of the photoredox cycle strongly depends on the control of the vectorial photoinduced electron transfer in the systems. *Tris*(2, 2'-bipyridine) ruthenium complex, $\text{Ru}(\text{bpy})_3^{2+}$, is one of the most well-known redox-active sensitizers. The charge transfer excited state of $\text{Ru}(\text{bpy})_3^{2+}$ is quenched by both electron acceptor and donor, yielding a powerful oxidant and reductant, respectively (eqs.(1) and (2)).



In this paper, photoinduced electron transfer of the chromophore, especially, bipyridine chelated ruthenium complex incorporated into PDDA polymeric LB film, is discussed.

EXPERIMENTAL

Ruthenium-containing copolymers were prepared as shown in the Scheme 1^[8, 9]. Firstly the copolymers of *N*-dodecylacrylamide (DDA) with 4-vinyl-4'-methyl-2, 2'-bipyridine (Vbpy) were prepared by a usual free radical polymerization in benzene at 60 °C with 2, 2'-azobis(isobutyronitrile) as a thermal initiator. The copolymers were purified by reprecipitation from filtered chloroform solution into a large excess of acetonitrile and dried under vacuum at room temperature. The copolymer composition was 21/1 = DDA/Vbpy, and its molecular weight was 5300. Secondly, the resulting copolymer (polymer bipyridine ligand) was refluxed in *n*-butanol/xylene solvent with bis-2, 2'-bipyridine ruthenium chloride ($\text{Ru}(\text{bpy})_2\text{Cl}_2$) to prepare *tris*-(bipyridine) ruthenium complex. The complex formation reaction was monitored by a decrease in absorbance at 540 nm due to $\text{Ru}(\text{bpy})_2\text{Cl}_2$ and an increase in absorbance at 450 nm characteristic of *tris* (bipyridine) ruthenium complex. The counter chloride anion was replaced with more hydrophobic PF_6^- anion by pouring the reaction mixture into a large excess of NH_4PF_6 methanol solution. The polymer ruthenium complexes were extracted with chloroform and then the chloroform was evaporated to give the final polymer complexes.



Scheme 1

RESULTS AND DISCUSSION

Monolayer and LB Multilayers Formation.

The properties of a monolayer floating on a water surface was investigated by a measurement of the surface pressure ($\pi = \gamma_0 - \gamma$) which is defined as the difference between the surface tension (γ_0) of pure water and the (γ) of the water covered with a monolayer. Figure 2 shows the $\pi - A$ isotherms of the ruthenium copolymers with varying ruthenium content which are spread from a chloroform solution on a water surface. The $\pi - A$ isotherms indicate that a stable condensed monolayer with a high collapse pressure is formed with the copolymer of N-dodecylacrylamide (DDA). The collapse pressure and the slope of rise in surface pressure decrease with the ruthenium content. The limiting surface area per monomer unit can be obtained to be $0.25 \sim 0.28 \text{ nm}^2$ by extrapolating the isotherms of the condensed state to zero pressure. The surface area for a surfactant ruthenium complex^[10] has been reported to be about 1.0 nm^2 , and we also have reported 1.2 nm^2 for a hydrophobic ruthenium complex in a mixed monolayer^[11]. The small surface area for the Ru complex in the present case means that the hydrophilic ruthenium complex head group enters into the water subphase.

The condensed polymer monolayers with the ruthenium content less than 0.12 mole fraction could be transferred onto solid supports such as quartz slide at both downward and upward stroke with a transfer ratio of unity, giving stable polymer Langmuir-Blodgett multilayers.

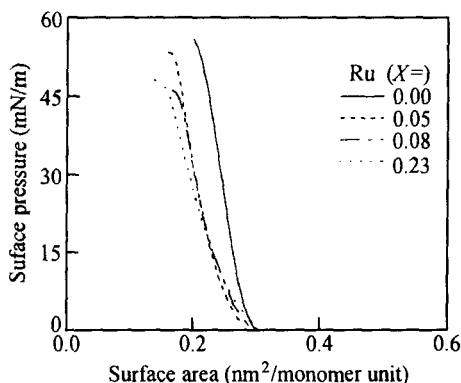


Fig.2 Surface pressure–area isotherms of DDA copolymers with various ruthenium contents at 19 °C

Electronic Absorption Spectra

The absorption spectra for the DDA-Ru polymer LB films are shown in Fig.3. The absorbance at 466 nm which is attributed to the MLCT (metal to ligand charge transfer) band of polybipyridyl ruthenium complex is plotted as a function of the number of deposited layers (Fig.4). A linear relationship was obtained even up to 300 layers with a slope of 4.4×10^{-4} (absorbance per layer), indicating the successive and regular deposition of the monolayer. This means that the ruthenium complex is dispersed molecularly along the polymer chain in the LB film, not forming aggregates. From the absorbance per layer (4.4×10^{-4}) for DDA-Ru(0.04) monolayer, we can calculate the two dimensional concentration of the Ru complex in the monolayer to be $3.1 \times 10^{-11} \text{ mol/cm}^2$, which is in fair agreement with the result calculated from the limiting surface area in the $\pi - A$ isotherms.

Redox Property

In order to investigate the redox property of the ruthenium in the LB film, cyclic voltammograms (CV) for the monolayer deposited on ITO electrode was measured (Fig.5). The CV of the monolayer of DDA-Ru copolymer showed an anodic peak at 1.1 V versus SCE, which corresponds

to the redox potential of $\text{Ru}^{2+/3+}$. The peak current was proportional to the scan rate (V), as expected from the equation, $i_p = n^2 C_r F^2 V / 4RT$ (where C_r is the surface concentration) derived for a cyclic voltammogram of diffusionless redox species in thin-layer cell. These results indicate that ruthenium-containing LB film is capable of working as a redox active film.

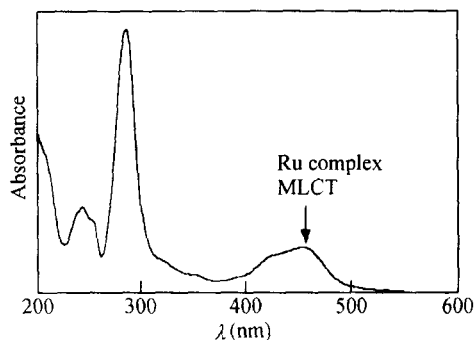


Fig.3 Electronic absorption spectrum of DDA-Ru copolymer in LB film

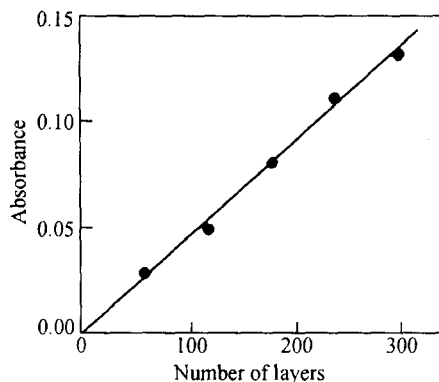


Fig.4 A linear relationship between the absorbance at 466 nm and the number of deposited layers

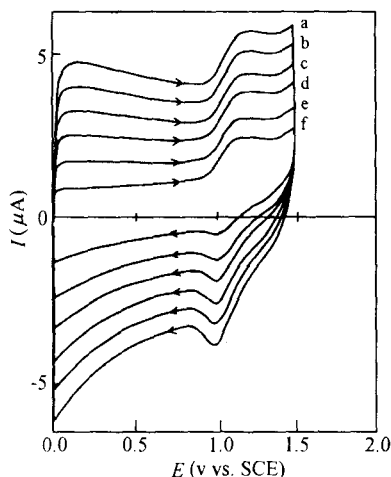


Fig.5 Cyclic voltammograms for the monolayer of DDA-Ru copolymer
Scan rate: a-f: 300, 250, 200, 150, 100, 50 mV/s, respectively

Photogalvanic Cell

As a potential application, the photogalvanic effect of the Ru-DDA monolayer deposited on metal electrode was investigated (Fig.6). On visible light irradiation on the monolayer deposited ITO electrode in contact with an aqueous solution containing an electron donor (thiol compound), a photoanodic current was observed to flow. The photocurrent showed a quick response to the switching of light on or off. The action spectrum of the photocurrent is in fair agreement with the absorption spectrum of the Ru complex (Fig.7). The current increases with the light intensity and the concentration of the thiol compound (electron donor). It is known that the excited state of polypyridyl ruthenium complexes are effectively quenched by thiol compound via electron transfer process^[11]. The photogalvanic cell is based on Ru^+ which is formed by the oxidative

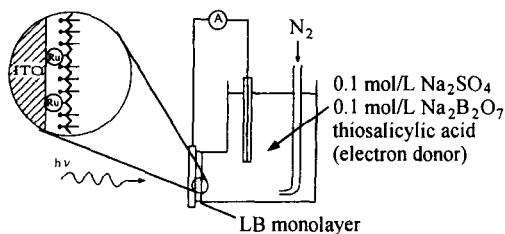


Fig.6 Electrochemical apparatus for measuring photogalvanic effect

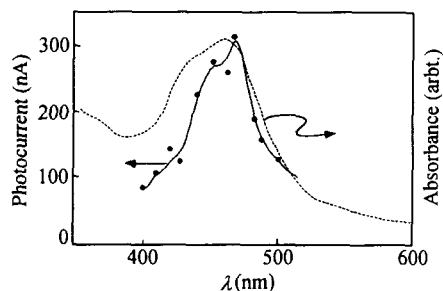


Fig.7 Action spectrum of photocurrent and the absorption spectrum of the ruthenium complex

quenching of Ru^{2+*} by electron donor (thiol); that is, the following mechanism (eqs. (3)~(5)) for photogalvanic effect in the monolayer can be proposed.



The LB monolayer has a thickness of about 1.8nm, which results in a high responsive current and the effective light energy conversion. A variety of applications using this photoredox LB multilayers is expected.

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