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Preparation of Ruthenium(II) Complex-Containing Polymer Monolayers and Langmuir-Blodgett Films

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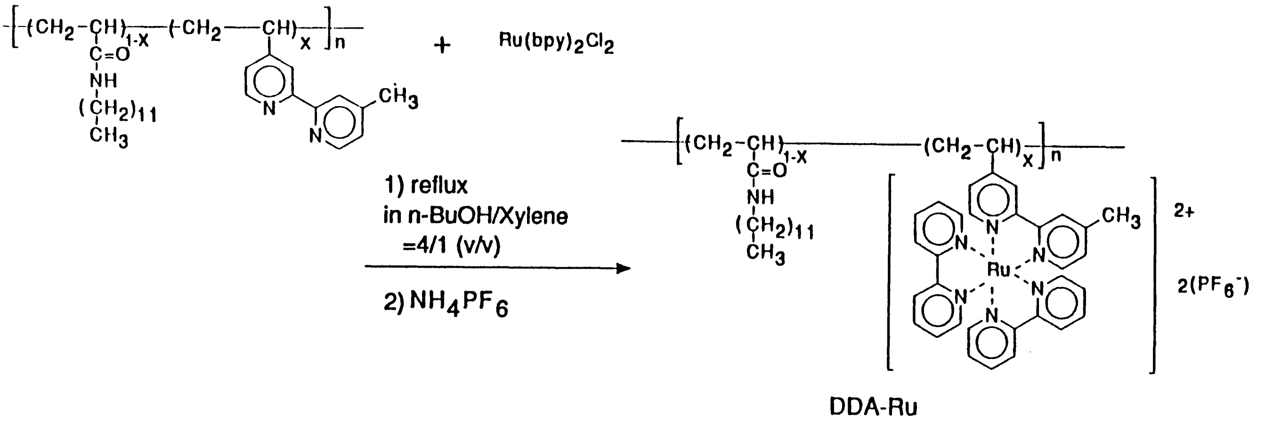
The copolymers of $[Ru(bpy)_2(Vbpy)]^{2+}$ and *N*-dodecylacrylamide (DDA) form a stable condensed monolayer on a water surface and the monolayers could be transferred onto solid supports, yielding the Y-typed (bilayer type) ruthenium (II) complex-containing polymer Langmuir-Blodgett (LB) films.

$Ru(bpy)_3^{2+}$ (bpy=2,2'-bipyridine) has received much attention as a redox-active sensitizer and the photoinduced electron transfer processes using this complex have been extensively investigated from the viewpoint of solar energy conversion.1-3) Especially the electron transfer in various molecular assemblies such as micelle, microemulsion, and polyelectrolyte has been studied for efficient photoenergy conversion.4-6) LB multilayer assembly offers more elaborate microenvironment with highly molecular orientation, different from that in random molecular assemblies. Some surfactant ruthenium complexes capable of forming monolayer have been prepared and the photochemical behavior has been also investigated aiming a photochemical cleavage of water with the assembly.7-9)

We have attempted to incorporate various photofunctional groups into polymer LB multilayer assemblies in the form of the copolymers of DDA which has an excellent ability to form monolayer and LB assembly.10) In this work, we have succeeded in the preparation of polymer LB films containing molecularly dispersed ruthenium complex. Described is the spreading behavior of the copolymers of *N*-alkylacrylamides and $[Ru(bpy)_2(Vbpy)]^{2+}$ (Vbpy=4-vinyl-4'-methyl-2,2'-bipyridine) on a water surface and some properties of the LB films.

Ruthenium-containing copolymers were prepared according to published procedure:[11,12] *N*-Alkylacrylamide (alkyl:dodecyl (DDA), tetradecyl (TDA), and octadecyl (ODA)) and Vbpy are copolymerized by a usual radical polymerization, and the resulting copolymer (polymer bipyridine ligand) is refluxed in n-buthanol/xylene solvent with bis-2,2'-bipyridine ruthenium (II) chloride ($Ru(bpy)_2Cl_2$), yielding the ruthenium copolymer (Scheme 1).



Scheme 1.

Figure 1 shows the surface pressure (π) - area (A) isotherms of the ruthenium copolymers which are spread from a chloroform solution on a water surface. The π - A isotherms indicate that the stable condensed monolayer with a high collapse pressure is formed with the copolymer of DDA. This is consistent with the results for the monolayer of poly(*N*-alkylacrylamides).[10a)] The π - A isotherms for the monolayer of DDA-Ru copolymers were measured with varying ruthenium content (X) (Fig. 2). The collapse pressure and the slope of rise in surface pressure decreased with the ruthenium content. The limiting surface area per monomer unit can be obtained to be 0.25 - 0.28 nm^2 by extrapolating the isotherms of the condensed state to zero pressure. The surface area for a surfactant ruthenium complex[8)] has been reported to be about 1.0 nm^2, and we also have reported 1.2 nm^2 for a hydrophobic ruthenium complex

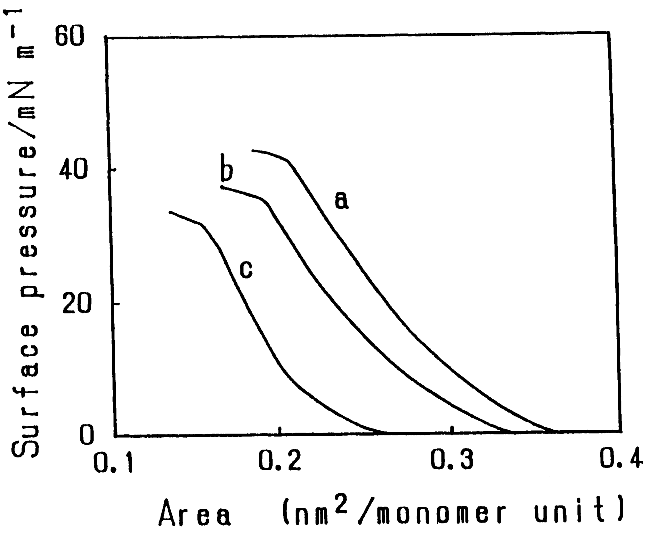


Fig. 1. Surface pressure-area isotherms of Ru complex-containing copolymers at 19 °C. a) DDA-Ru, b) TDA-Ru, c) ODA-Ru copolymer.

in a mixed monolayer.9) The small surface area for the Ru complex in the present case means that the hydrophilic ruthenium (II) complex head group enters 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 strokes with a transfer ratio of unity. The absorbance at 466 nm which is due to the MLCT (metal to ligand charge transfer) band of polypyridyl ruthenium complex is plotted as a function of the number of deposited layers (Fig. 3). The linear relationship was obtained with a slope of 1.47 x 10^{-3} (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. The absorbance per layer (1.47 x 10^{-3}) for DDA-Ru (0.12) monolayer corresponds to a molar extinction coefficient (ε) of 1.9 x 10^4 ($M^{-1}cm^{-1}$). This value nicely agrees with ε (1.4 x 10^4 $M^{-1}cm^{-1}$) of Ru(bpy)$_3^{2+}$ in solution[13], considering the difference between in solid and in solution. The molecularly dispersion of ruthenium chromophore is supported also by the emission and the excitation spectra (Fig. 4). Both spectra are in fair agreement with those for Ru(bpy)$_3^{2+}$. As a preliminary experiment, kinetic analysis for the emission decay of the

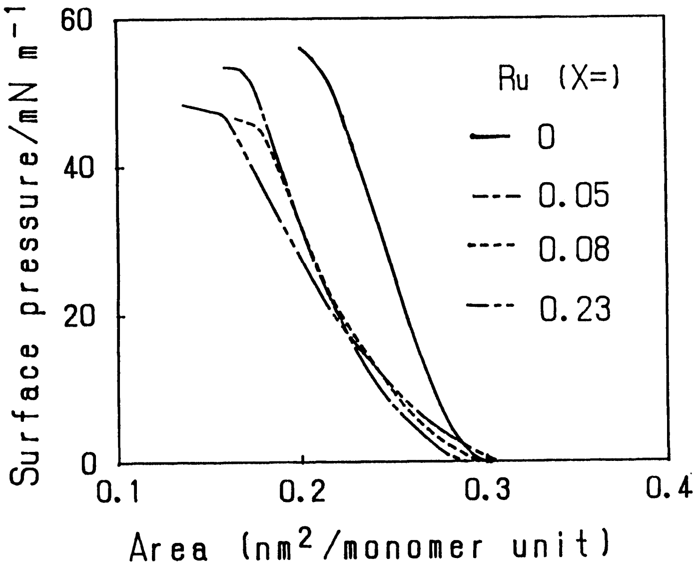


Fig. 2. Surface pressure-area isotherms of DDA-Ru copolymers with various Ru contents (X) at 19 °C.

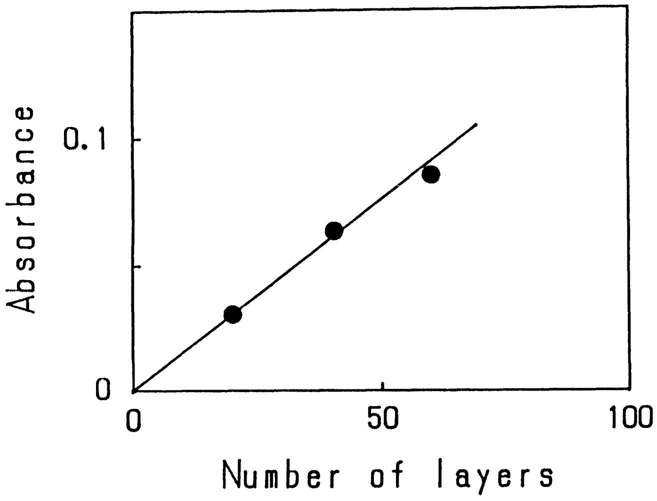


Fig. 3. Absorbance change at 466 nm with the number of DDA-Ru(0.12) monolayers deposited.

ruthenium chromophore in the polymer LB film was carried out by means of the laser photolysis technique. The emission decay consists of two lifetimes with 28 ns (80%) and 200 ns (20%). The detailed photochemical behavior of the ruthenium chromophore in this LB assembly is currently undertaken. This LB film is expected to be applied to various photofunctional devices.

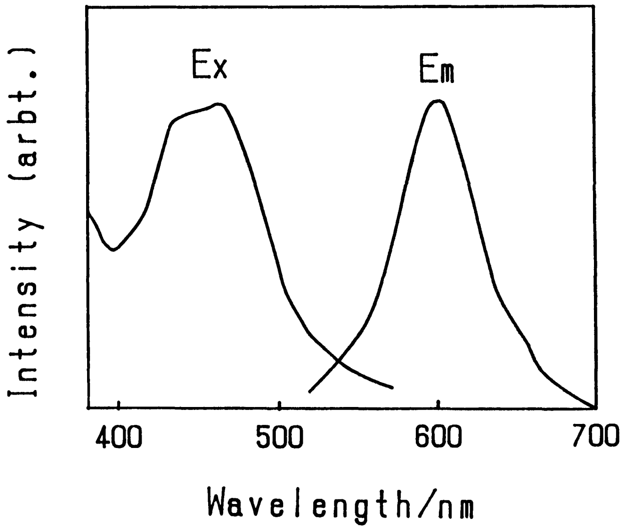


Fig. 4. Emission and excitation spectra of DDA-Ru(0.12) LB film (10 monolayers).

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