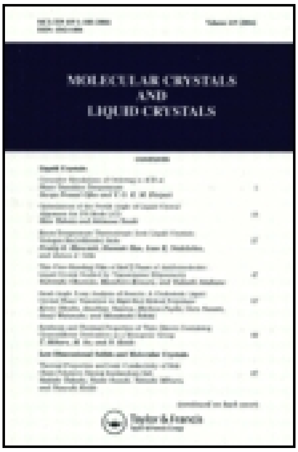

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Langmuir Monolayers and Langmuir-Blodgett Films of Mixtures of Polyaniline and a Ruthenium Complex, mer[RuCl 3 (dppb)(py)]

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Langmuir Monolayers and Langmuir-Blodgett Films of Mixtures of Polyaniline and a Ruthenium Complex, mer-[RuCl$_3$(dppb)(py)]

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ABSTRACT

Strong interaction at the molecular level has been observed in Langmuir monolayers of polyaniline and a biphosphinic ruthenium complex, named Rupy. The area per molecule and maximum surface potential for the mixed films varied non linearly with the relative concentration of Rupy. Y-type Langmuir-Blodgett films have been deposited from the mixtures. Upon increasing the amount of Rupy, the LB films become increasingly oxidized, causing a blue shift in the peak attributed to the quinoid species of the PANI UV-visible spectra.

Keywords: polyaniline; ruthenium complex; LB films; spectroscopy UV

INTRODUCTION

The Langmuir-Blodgett (LB) technique has been employed with a variety of non-amphiphilic materials in recent years, particularly conducting polymers. This has been made possible through the development of various strategies to render such materials

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processible[1]. With this flexibility one may now envisage the formation of supramolecular structures involving more than one material, which is advantageous because distinct properties of the materials may be combined while retaining the capability of molecular control. In this paper we exploit one of such new possibilities, and investigate the film formation properties of mixtures of a conducting polymer, PANI, and a biphosphinic ruthenium complex, viz. *mer*-[$RuCl_3$(dppb)(py)] (dppb=1,4-bis(diphenylphosphine)buthane, py = pyridine) (Rupy).

EXPERIMENTAL DETAILS

Rupy, whose structure is shown in the inset of Fig. 1c, was synthesized according to the procedures described by Wohnrath et al.[2] and dissolved in chloroform. PANI was synthesized chemically using the method described by Mattoso et al[3]. Spreading solutions for PANI were prepared by dissolving 1 mg in 1.3 mg of camphor sulfonic acid (CSA), 1 mL of m-cresol and 10 mL of chloroform, with the mixture being kept under sonication for ca. 2 hours. This mixture was then filtrated to remove non-dissolved PANI. Monolayer experiments and LB transfer were conducted with a KSV5000 system, in a class 10,000 clean room. Monolayers of the pure Rupy and PANI and their mixtures were spread on an acidic subphase (pH = 2) and compressed at a barrier speed of 10 mm/min. The LB films were transferred onto indium tin oxide-coated glass (ITO, from Asahi Co., Japan) or quartz substrates, with a typical dipping speed of 3 mm/min. Transfer was of Y-type, and conducted at a fixed surface pressure of 17 mN m^{-1} for pure PANI and mixed PANI-Rupy films, and 15 mN m^{-1} for Rupy. The transfer ratio was typically 0.9 in the upstrokes and 0.7 in the downstrokes. UV-vis. absorption measurements were carried out in a HITACHI U-2001 spectrophotometer.

RESULTS AND DISCUSSION

Langmuir monolayers and LB films from PANI-Rupy

Figures 1a and 1b show the surface pressure and surface potential isotherms for monolayers of the various mixtures of PANI and Rupy and pure PANI spread on an acidic subphase. The curve for the pure Rupy is not shown. The acidic subphase was chosen because PANI and

Rupy form more stable monolayers under such condition. The low areas of ca. 30 Å^2 (Rupy) and 12 Å^2 (PANI) per molecule, obtained by extrapolating the high-pressure region of the isotherms to zero pressure, indicate that both pure PANI and Rupy form non-monomolecular structures on an aqueous subphase. This is known for PANI from previous studies[4-7], and it is not surprising for Rupy either owing to its semi-amphiphilic nature. The area of ca. 30 Å^2 for Rupy is certainly much smaller than expected, as the molecule cross section is ~140 Å^2 according to the CPK model using the Hyperchem program[8]. The incorporation of Rupy into the mixed monolayer is clearly illustrated in Figure 1b by the shift towards larger areas per polyaniline monomer as the relative concentration of Rupy increased. Such an incorporation does not occur in separate domains, unlike the case of polyaniline and cadmium stearate monolayers[4]. When domain separation occurs, the area per molecule of the mixed monolayer – now in terms of both components - increases linearly with the concentration of the component with larger area, and this is not the case for PANI+Rupy monolayers, as shown in Figure 1c. The shape of the curve is characteristic of repulsion between the components in the mixture. This interaction at the molecular level is also manifested in the surface potential results. Taking the maximum surface potential from each curve of Figure 1a, one obtains the plot against the Rupy relative concentration in Figure 1c, whose shape is similar to that of the area dependence. Another worth noting feature is the high surface potential for Rupy, which probably points to the existence of groups with large dipole moments.

A quantitative treatment of the surface potential data cannot be performed at this time for macromolecular systems such as the one investigated here. Nevertheless, the shape of the surface potential does provide useful information. The curves in Fig. 1c are similar to most monolayers, for which there is no drastic molecular rearrangement during compression. The increase in potential at a given area per molecule is caused by the coming together of microdomains, which then make the surface potential detectable by the probe. Fig. 1c also shows that for most monolayers the surface potential was already non-zero when the compression started, which means that large domains were present immediately after spreading. As indicated by the non-linear dependence of the area and potential with the amount of Rupy, these domains were not separate domains of Rupy and PANI, but rather involved the two components in a given single domain.

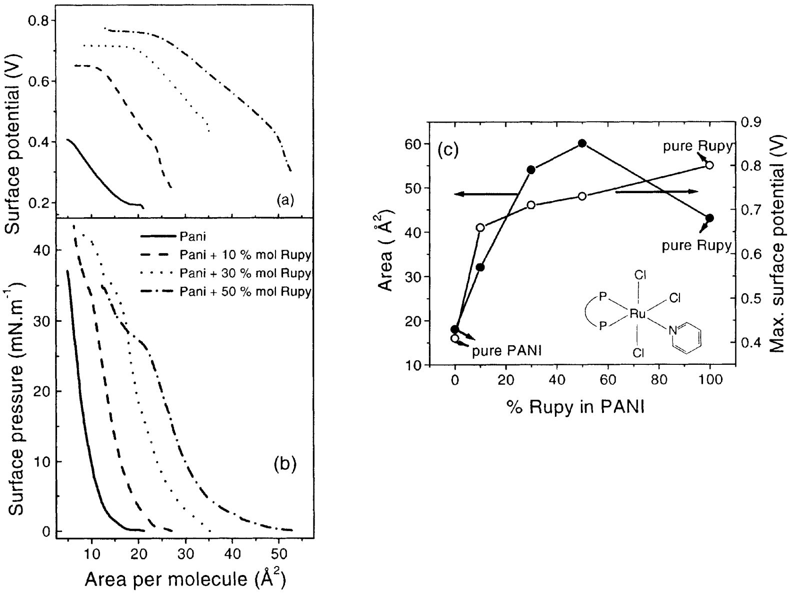

FIGURE 1 (a) ΔV-A isotherms and (b) π-A isotherms for mixed PANI-Rupy monolayers on HCl pH 2 subphases. The abscissa brings the area per monomer of Pani. (c) maximum surface potential (open circles) and extrapolated area per molecule (solid circles) vs. mol% of Rupy in the mixed monolayers. Rupy structure is presented in the inset

Characterization of PANI-Rupy LB films

The UV-vis. absorption spectra of a 61-layer PANI LB film and 61-layer mixed (PANI-Rupy) LB films on quartz substrates are shown in Fig. 2. For pure PANI, a broad band appears centered at 810 nm, which indicates that the partially oxidized PANI (emeraldine form) is doped, as one should expect since the monolayers were transferred from an acidic subphase. The pure Rupy LB film displays a band centered at approximately 660 nm. In the mixed films, the incorporation of the Rupy complex causes a blue shift in the PANI band to ca. 790, 725 and 720 nm for 10, 30 and 50 mol% of Rupy, respectively. This shift could be caused either by partial dedoping of PANI or by a change in its oxidation state as the 810 nm band is associated with quinoid species.

Further experiments where absorption spectra were taken for LB films under applied potentials (not shown) indicated that the increase in oxidation is the cause for the blue shift. These spectra were obtained for LB films onto ITO substrates, under applied electric potentials varying from –0.3 to 0.1 V. For pure PANI, the band at large wavelengths increases with increasing applied potentials as the degree of oxidation of PANI is altered. In the mixed film with 30mol% of Rupy, the spectra are practically insensitive to the electric potential because the degree of oxidation had already been increased by the incorporation of Rupy. Such an increase in oxidation is corroborated by spectrochemical analysis[8], where the incorporation of Rupy in the mixed LB films induced a gradual loss of electroactivity of PANI due to oxidation. For example, for the mixed film with 50mol% Rupy no electroactivity could be detected.

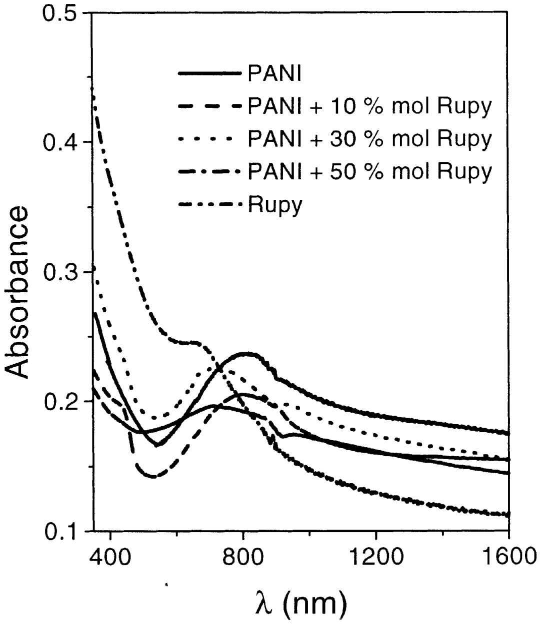

FIGURE 2 UV-vis absorption spectra of 61-layer LB films produced from pure PANI, pure Rupy and mixed films.

CONCLUSIONS

Surface pressure and surface potential measurements have been presented for the metallic complex, Rupy, which forms non-monomolecular structures when spread on an acidic subphase, and can also be incorporated in polyaniline (PANI) monolayers. Strong interaction between Rupy and PANI, at the molecular level, cause the area per molecule and the surface potential to vary non linearly with the amount of Rupy in the mixed films. Such an interaction was attributed to oxidation of PANI, induced by Rupy, which also affected the UV-vis. absorption spectra of deposited LB films.

Acknowledgments

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