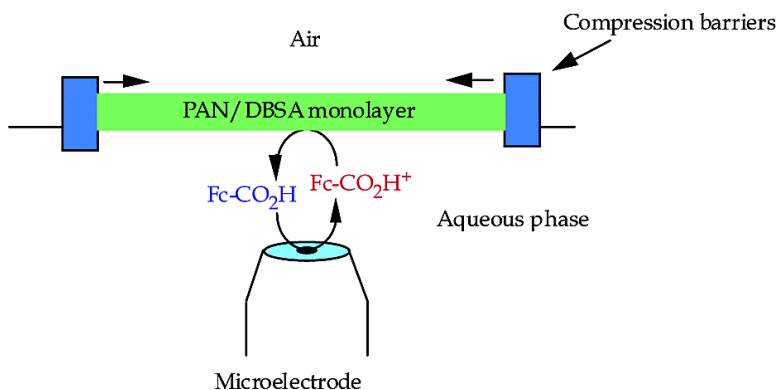


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J. Am. Chem. Soc., **2003**, 125 (31), 9312-9313 • DOI: 10.1021/ja036146q • Publication Date (Web): 15 July 2003

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Effect of Surface Pressure on the Insulator to Metal Transition of a Langmuir Polyaniline Monolayer

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Electronically conducting polymers, such as polypyrrole and polyaniline, are envisaged to replace some of the metal- and metal-oxide-based components in micro- and nanoelectronics.¹ Moreover, this class of material has considerable potential for applications as diverse as light-emitting diodes,² photovoltaic devices,³ and microactuators.⁴ These applications, and others, require an understanding of the electronic characteristics of ultrathin conducting polymer films.^{5,6} Monolayers of conducting polymers are readily formed by spreading organic-soluble polymers at the water/air interface following the Langmuir method.^{7–9} In most studies, the monolayers have been deposited layer by layer onto a solid support to form Langmuir–Blodgett films for further characterization or application.

Evidently, the conductivity of these thin films cannot be measured easily in-situ, that is, while spread on a Langmuir film balance, but rather after transfer to a solid support. This makes it difficult to address the fundamental question of how surface pressure and organization influence the lateral conductivity of such films, particularly because segregation effects may compromise the structural integrity of monolayers on solid supports.¹⁰ There have been previous studies on bulk materials in the solid-state, where the influence of pressure on conductivity has been explored,^{11,12} but in conducting polymers the effects are usually small and a clear insulator–metal transition, as a result of pressure, has not previously been seen.

Here, we report the first in-situ detection of an insulator to metallic transition of a Langmuir polyaniline (PAN) monolayer as a result of gradually changing the surface pressure. This has been accomplished using a scanning electrochemical microscope (SECM).¹³ With this approach, a biased microelectrode generates a flux of electroactive species, which may undergo a redox reaction at the target interface (PAN monolayer), the extent of which depends on the surface conductivity.

SECM has recently targeted thin films at the water/air interface,¹⁴ following earlier work using contacting microelectrodes,¹⁵ and here we build on this methodology to measure surface conductivity of a monolayer. Specifically, we use an inverted 25 μm diameter Pt microelectrode to approach a Langmuir film of PAN (Figure 1). The film was spread (0.2 mg mL⁻¹ PAN and dodecylbenzenesulfonic acid in a 2:1 molar ratio of the aniline unit and the acid) from a 9:1 (v/v) mixture of chloroform and *m*-cresol. The aqueous subphase contained 0.1 mM ferrocene monocarboxylic acid (Fc-CO₂H) and 0.03 M HCl, ensuring that the PAN monolayer was in the protonated (doped) emeraldine state.

Figure 2a shows the surface pressure–mean molecular area isotherm of a PAN monolayer. The mean molecular area was based on the emeraldine salt repeat unit with a formula weight of 362. A monotonic increase of the pressure up to 45 mN m⁻¹ is followed by a moderate pressure–area slope. Finally, the film collapses as is evidenced by noise on the isotherm and confirmed by simulta-

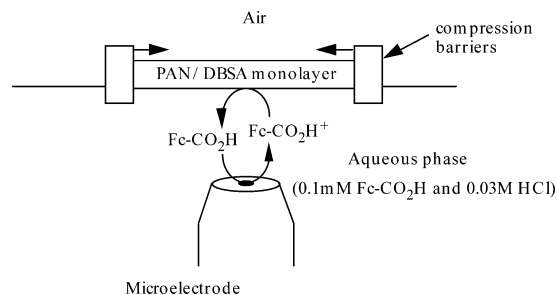


Figure 1. Schematic (not to scale) of the SECM configuration for measurements of the conductivity of a PAN Langmuir monolayer.

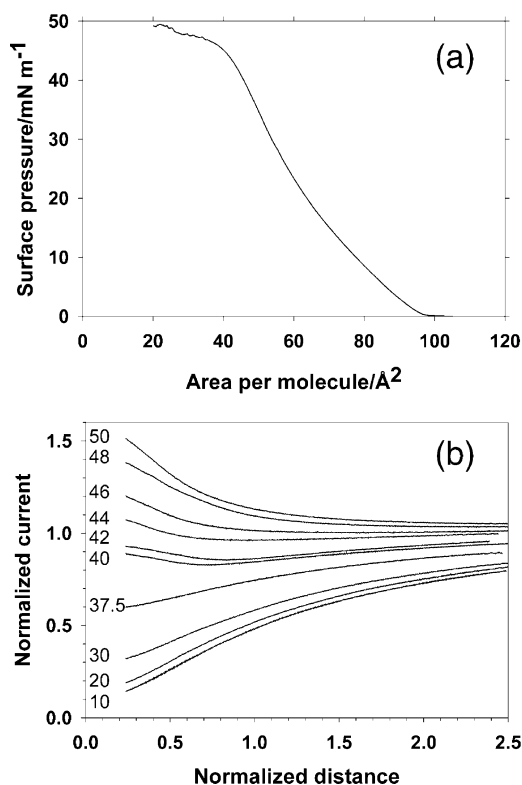


Figure 2. (a) Isotherm of surface pressure as a function of the mean area per repeat PAN unit on a 0.03 M HCl subphase. (b) Normalized current versus normalized distance approach curves for the oxidation of Fc-CO₂H at a 25 μm diameter Pt microelectrode (0.45 V vs Ag wire) approaching a PAN monolayer interface. Surface pressures are defined on the figure in units of mN m⁻¹. The microelectrode was withdrawn from the interface when the surface pressure was changed.

neous Brewster angle microscopy. Below the collapse point, the monolayer was entirely homogeneous.

The conductivity at selected surface pressures was investigated by SECM feedback mode approach curves.¹⁶ Figure 2b represents the normalized current–distance approach curves¹⁷ acquired by

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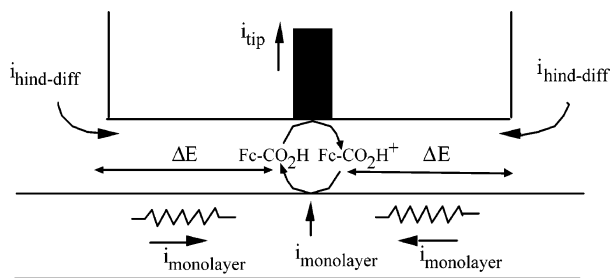


Figure 3. Schematic diagram showing the charge transport processes occurring in the SECM feedback experiment. ΔE refers to the potential difference at the PAN surface induced by the concentration variations of the redox species in solution.

moving the microelectrode toward the water/air interface while generating $\text{Fc-CO}_2\text{H}^+$ from the oxidation of $\text{Fc-CO}_2\text{H}$ (Figure 1) under diffusion-controlled conditions. The distance was determined by fitting the approach curve obtained in the absence of a PAN monolayer with the theoretical negative feedback (hindered diffusion) curve,¹⁶ as described previously.¹⁴ It is evident that the surface pressure has a distinct effect on the tip current. While at low surface pressures the steady-state current decreases as the microelectrode–monolayer distance decreases (tending to the negative feedback response of an insulating surface), at elevated surface pressures the feedback current increases (positive feedback) as the distance between the microelectrode and the monolayer decreases.

The tip current is affected by two processes:¹⁶ the hindrance of $\text{Fc-CO}_2\text{H}$ diffusion to the microelectrode while approaching the interface, which causes a decrease of the current, and the regeneration of the electroactive species at the interface, which results in an increase of the current. The regeneration of the electroactive species can be driven by high surface conductivity, even when the interface is not connected to an external power source,¹⁸ or by an oxidation–reduction process of the surface.¹⁹ The latter can be ruled out due to the redox potential of the mediator, that is significantly more positive than the doping/undoping process of the PAN monolayer.²⁰ The fact that the feedback current changes from negative to positive as a function of surface pressure is therefore due to an insulator to conductor transition that is caused by compressing the film.

Inspecting the approach curves (Figure 2b) more closely reveals that the current response deviates from essentially hindered diffusion characteristics only at pressures above 20 mN m^{-1} , with significant positive feedback contributions above 40 mN m^{-1} . This behavior cannot be directly correlated with a phase transition of PAN. The nature of the change of the insulator to metal transition suggests that the conductivity is more likely to be related to the decrease in distance between the PAN chains with monolayer compression, because interchain transfer is a possible rate-limiting process controlling conductivity.²¹

Lateral charge propagation in the monolayer in the SECM experiments is driven by the potential difference, established by variations in the concentration of the redox couple (Nernst relation) in the gap between the tip and the monolayer (Figure 3). This diffusion problem is readily treated by numerical simulation and establishes the relationship between the distance, the potential difference, ΔE , and tip current. The measured tip current, i_{tip} , is the sum of two contributions: the component due to hindered diffusion of $\text{Fc-CO}_2\text{H}$, i_{hind} (which is known), and the current through the monolayer, $i_{\text{monolayer}}$, which is therefore readily deduced. Linear relationships were obtained between ΔE and $i_{\text{monolayer}}$ for each of the approach curves in Figure 2b, indicating that the tip current is largely controlled by the ohmic resistance of the film. The conductivity of the film (for each surface pressure) was then

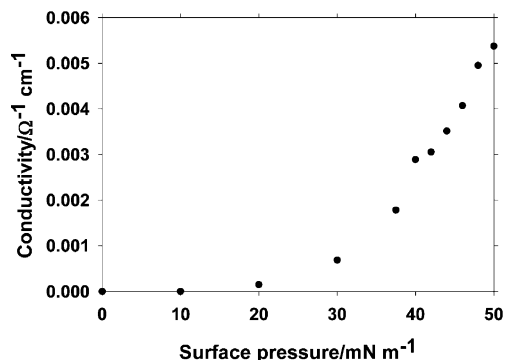


Figure 4. Conductivity of a PAN monolayer as a function of surface pressure.

calculated taking into account the cylindrical geometry and the film thickness (3.2 nm),²² determined by AFM and XPS after transferring the sample to a glass slide as a Langmuir–Blodgett film.

The results of this treatment are summarized in Figure 4, which shows the monolayer conductivity as a function of surface pressure. A remarkable increase in the conductivity is seen, beyond a threshold pressure of ca. 20 mN m^{-1} , demonstrating that ultrathin 2D conducting polymer systems must be highly compact to promote the most efficient lateral charge propagation.

Acknowledgment. We thank the EPSRC (GR/R73089) for a Visiting Fellowship for D.M.

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JA036146Q