Preparation and Properties of Conducting Arachidic Acid/Polypyrrole Composite Langmuir–Blodgett Films

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SYNOPSIS

Electrically conducting arachidic acid/polypyrrole (PPy) composite films were prepared by exposing the arachidic acid LB films containing ferric chloride to pyrrole vapor. The optimum conditions to deposit matrix LB film were the subphase temperature of 23–25°C, pH of 6.0 and ferric chloride concentration of 5.0×10^{-5} M. The formation of PPy in the arachidic acid matrix LB films was confirmed by UV-visible spectra, FTIR spectra, and scanning electron micrographs. The average thickness of the composite LB films prepared at 0°C was 1525 Å. The composite films prepared at lower temperatures have more uniform surface and exhibit higher electrical conductivity than the films prepared at higher temperatures do. The in-plain conductivity and the transverse conductivity of the composite film were 10^{-3}–10^{-2} S/cm and 10^{-6} S/cm, respectively, and, thus, the conductivity anisotropy was about 10^3. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The Langmuir–Blodgett (LB) technique represents one of the few methods by which organic films of controlled thickness, uniform surface, and highly ordered structure may be deposited onto a substrate. The use of this method to deposit films of electroconductive materials shows a great promise for the applications in electronics and microdevices; thus, considerable efforts have been made towards the fabrication of highly anisotropic, ultrathin, semiconducting films.[1,2] Unfortunately, however, these LB films with low molecular amphiphilic compounds show poor stability, which has limited their application to practical devices. In order to improve the stability, efforts have been focused on the preparation of polymerized LB films.

Polypyrrole (PPy) is one of polymers with the most promising combination of environmental stability and high conductivity. In order to manipulate the electroconductive PPy into LB films, a number of different approaches have been adopted.[1,2] The approaches can be divided into three major types:

(1) the electropolymerization of amphiphilic pyrrole derivatives,[1] (2) the direct polymerization of pyrrole with a surface active derivative at the air–water interface of the trough,[1] and (3) the modification of preformed LB films by exposing to gaseous pyrrole.[2] The solid state reactions of LB films, such as the method (3) have the advantage of altering the chemical structure of the film without adversely affecting the molecular order.[3,4]

In this article, we report our findings obtained from the systematic investigation of the effect of preparation conditions on the morphologies, the surface wettability, and electrical properties of electroconductive arachidic acid/PPy composite LB films.
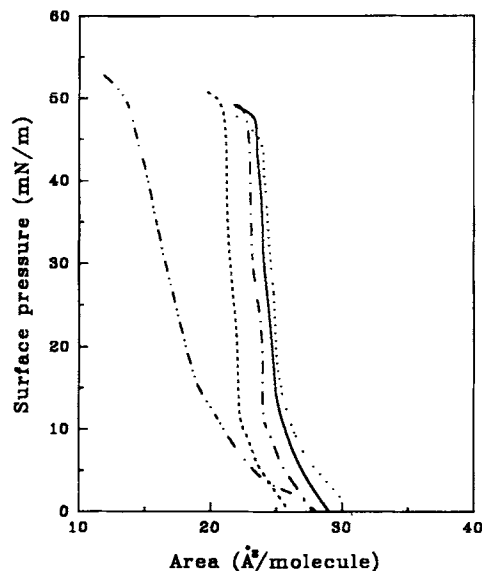
EXPERIMENTAL

Trough and Deposition Conditions for LB Films

A moving wall-type LB trough consisting of a moving wall, a barrier, a motor, and a dipper was made in our laboratory.

Surface pressure(p)–area(A) isotherms were found from Wilhelmy method.[5]

A piece of G7 grade filter paper with 8 mm width was used as a Wilhelmy plate and placed in front of

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Figure 1 π-A isotherms of ferric arachidate monolayers as a function of the subphase pH; (a) 3.3 (· · ·); (b) 4.2 (—); (c) 5.15 (- · -); (d) 6.05 (- – -); and (e) 7.4 (- · · -).

the moving barrier. The subphase pH was adjusted by the addition of either 0.1N HCl or 0.1N NaOH solution. The glass and quartz substrates were etched with concentrated KOH–ethanol solution and then rinsed with the deionized water in an ultrasonic cleaner (Branson 2200). A monolayer film was compressed to a surface pressure of 30 mN/m with the deposition rate of 10 mm/min at the subphase temperature of 23°C.
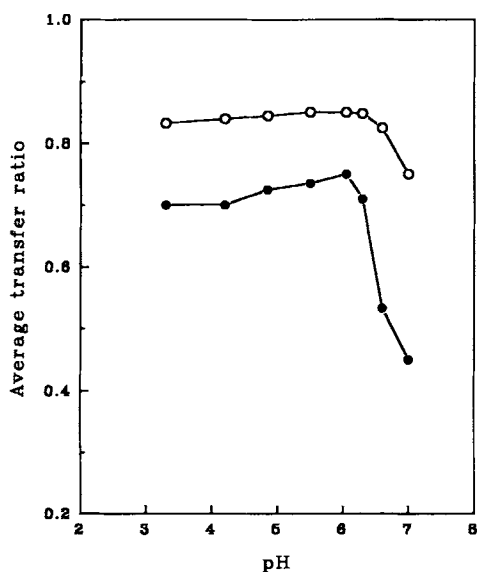

Figure 2 Average transfer ratio of ferric arachidate monolayer as a function of subphase pH; (a) out-stroke (O) and (b) in-stroke (●).
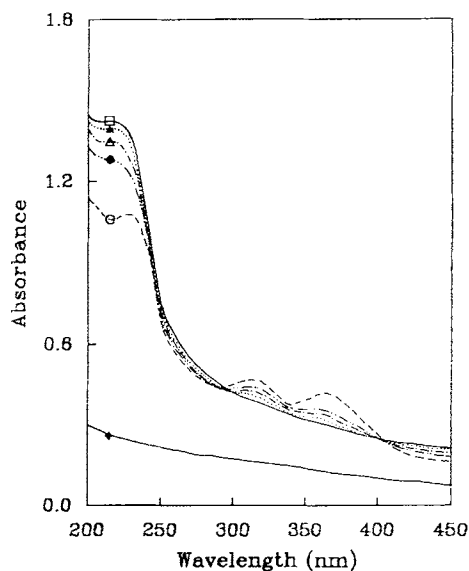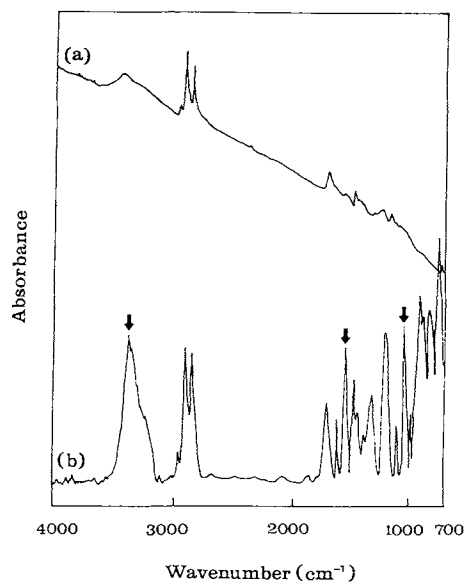

Figure 3 UV-visible absorption spectra of (a) ferric arachidate LB film (♦), (b) arachidic acid LB film containing FeCl₃ (O), and arachidic acid/PPy composite films prepared by exposing the sample (b) to pyrrole vapor for (c) 5 min (●), (d) 10 min (△), (e) 15 min (▲), and (f) 20 min (□).

Preparation of Arachidic Acid/PPy Composite Films

Multilayer thin films of ferric arachidate are formed from monolayers created by spreading a solution of
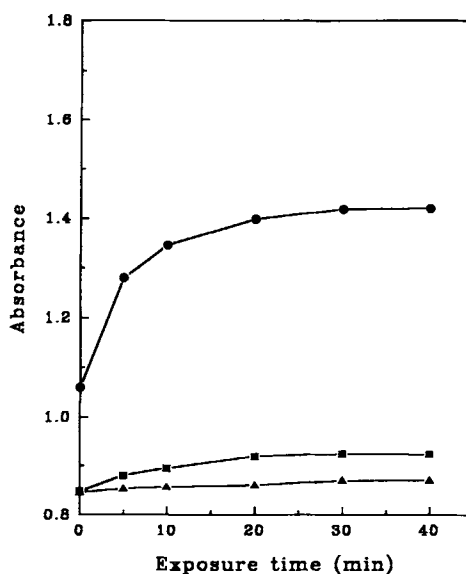
Figure 4 UV-visible absorption intensity at 215 nm as a function of exposure time to pyrrole vapor for the arachidic acid LB films containing (a) BaCl₂ (▲), (b) CdCl₂ (■), and (c) FeCl₃ (●) at 25°C.

Figure 5 FT-IR absorption spectra of (a) arachidic acid LB film containing $FeCl_3$ and (b) arachidic acid/PPy compisite film.

$1.0 \times 10^{-3}M$ arachidic acid in chloroform onto a subphase of high purity water (resistivity: 18 MW cm) containing various concentrations of ferric chloride (1.0×10^{-5}–1.0×10^{-3} M). The preformed multilayer thin film is then exposed to HCl vapor in order to convert the ferric arachidate into arachidic acid and ferric chloride. The released ferric chloride is now capable of polymerizing pyrrole monomer into electrically conductive PPy. Thus, the final step involves exposing the arachidic acid film containing ferric chloride to pyrrole vapor in a reaction chamber used by previous works[6,7] under a static vacuum of 60 Torr at temperatures ranging from 0 to 50°C. The pyrrole vapor diffuses into the multilayer structure and is oxidatively polymerized by the impregnated ferric chloride.

Measurement of Electrical Conductivity

A device structured with $Al/Al_2O_3/$composite LB film/ Al was used in order to measure the electrical properties of the composite LB films. The composite LB film was deposited on the bottom electrode prepared by the evaporation of Al onto a slide glass substrate. The aluminum oxide layer was inserted by dipping Al/glass substrate in LB trough and the thickness of aluminum oxide layer was taken to be 30 Å according to Madden et al.[8] The electrical conductivities were estimated by using following relations.[9]

$$\sigma_\perp(\mathrm{S/cm}) = \frac{d_{ox} + d}{RA}$$

$$\sigma_\parallel(\mathrm{S/cm}) = \frac{d_{gap}}{R|d}$$

where $\sigma_\perp$ and $\sigma_\parallel$ are the transverse and the in-plane conductivities, d_{ox} and d are the thickness of aluminum oxide layer and LB film, respectively, R is the resistance value, A is the area of the electrode, d_{gap} is the distance between electrode and | is the width of the electrode.

Other Characterizations

The formation of PPy in the composite LB films has been identified from the plot of the UV-Visible absorbance at 215 nm vs. the exposure time. UV-Visible spectra were measured by utilizing Shimadzu
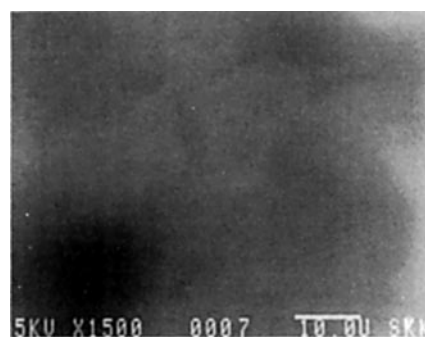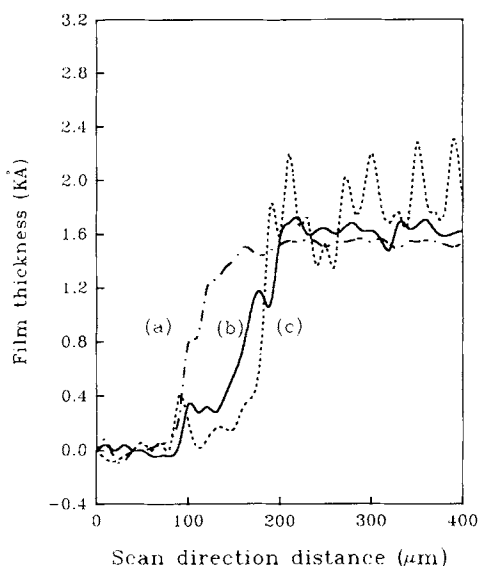

(a)
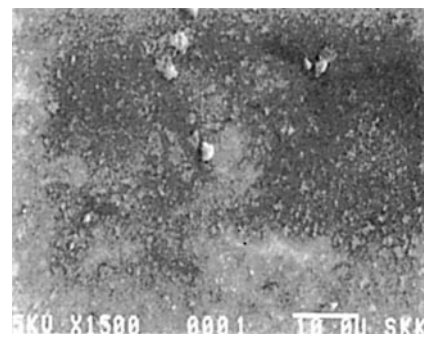
(b)

Figure 6 Scanning electron micrographs of (a) arachidic acid LB film containing $FeCl_3$ and (b) arachidic acid/PPy composite films prepared by exposing the sample used for (a) to pyrrole vapor for 20 min at 25°C.

Figure 7 Film thickness of arachidic acid/PPy composite films prepared by exposing the sample used for Figure 8(a) to pyrrole vapor for 20 min at (a) 0°C (b) 25°C, and (c) 50°C.

UV-Visible spectrophotometer UV-240. FTIR spectra were recorded on a Unicam Mattson 5000 IR spectrophotometer. The film thickness of arachidic acid/PPy composite LB films was measured by using a mechanical probe (α-step, Aju Exim). The force applied to the stylus of α-Step was 6 mgf. The surface morphology of the films was observed by JEOL JSM-35 CF scanning electron microscope at an accelerating voltage of 5 or 15 KV.

RESULTS AND DISCUSSION

For the investigation of the spreading behavior of ferric arachidate on the water subphase the π-A isotherms were exhibited as a function of the subphase pH in Figure 1. All isotherms have shown a monotonous increase of surface pressure up to a collapse pressure. The limiting area A_o, which is estimated by extrapolating the maximum slope of the π-A isotherm to zero surface pressure, decreases with the increase of the subphase pH by forming a more closely packed monolayer, and the slope of the π-A isotherms also decreases with the increase of the subphase pH. This may be due to the ionization of arachidic acid, which has resulted in the accelerated dissolution of the monolayer into the subphase.

Figure 2 represents the average transfer ratio for 11 strokes of ferric arachidate monolayer as a function of the subphase pH. At pH values of less than

about 6.4, a constant deposition has occurred on both in-stroke and out-stroke, and the optimum subphase pH for the deposition of the most effective ferric arachidate monolayer was 6.0 ± 0.1. At pH values of above 6.4, a decrease of average transfer ratio was observed. It is supposed that this phenomenon is due to the considerable increase in the viscosity of the ferric arachidate monolayer at higher pH values.[10] Figure 3 shows the typical UV-Visible spectra of ferric arachidate, arachidic acid with ferric chloride, and arachidic acid/PPy composite LB films at 25°C. The absorbance peak at 230 nm is due to the —COOH group of arachidic acid. It is believed that the absorbance peaks at 315 and 365 nm are due to the charge transfer absorption by the Fe^{3+}/chlorine complex. Absorption of a photon results in the transfer of an electron from the chlorine ion to an orbital associated with the Fe^{3+} ion. As the exposing time to pyrrole vapor becomes longer for the sample of Figure 3(b), the peak intensities at 315 and 365
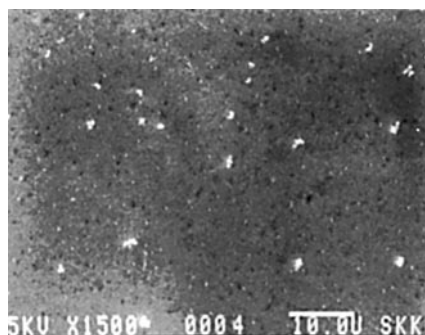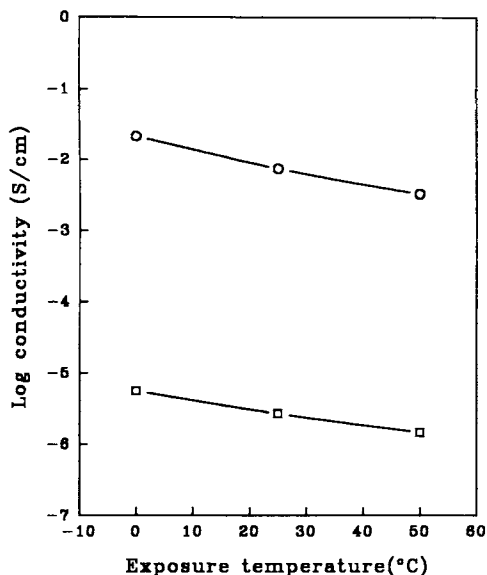

(a)
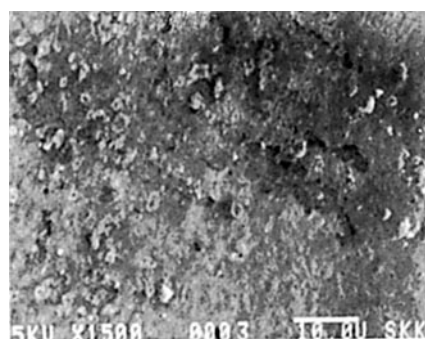
(b)

Figure 8 Scanning electron micrographs of arachidic acid/PPy compisite films prepared by exposing the sample used for Figure 8(a) to pyrrole vapor for 20 min at (a) 0°C and (b) 50°C.
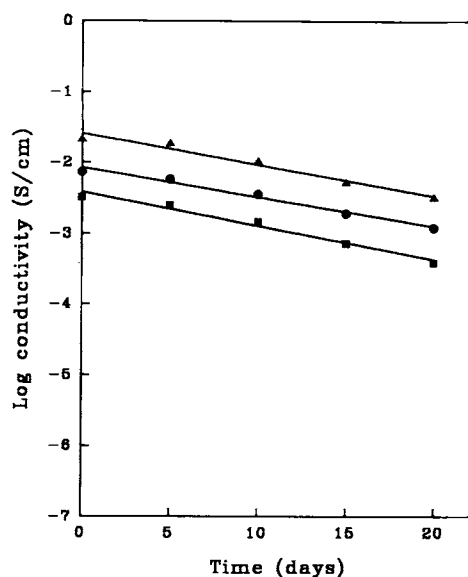
Figure 9   In-plain conductivity (O) and transverse conductivity (□) of arachidic acid/PPy composite LB films as a function of exposure temperature to pyrrole vapor (exposure time: 20 min).

Figure 10   Log conductivity vs. exposure time to ambient air for arachidic acid/PPy composite films, exposure temperature to pyrrole vapor; 0°C (▲), 25°C (●), and 50°C (■).

nm decrease while the characteristic band of PPy at 215 nm increases rapidly, as shown in Figure 3(c–f). This implies that as the exposing time to pyrrole vapor is longer the more PPy is synthesized by $FeCl_3$ and, consequently, the concentration of $FeCl_3$ in the composite LB films decreases.

In order to investigate the efficiency of the oxidizing agents, the arachidic acid LB films containing $BaCl_2$, $CdCl_2$, and $FeCl_3$ were respectively exposed at 25°C to pyrrole vapor. Figure 4 represents the relationship between the UV-Visible absorption intensity at 215 nm of each LB film and the exposure time to pyrrole vapor. It is evident that $FeCl_3$ is the most powerful oxidizing agent to produce electroconductive PPy with high yield.

FT-IR spectra of the samples used for Figure 3(b) and (f) are shown in Figure 5(a) and (b). The absorption peaks at 3380, 1540, and 1040 cm^{-1} marked by an arrow in Figure 5(b), are the characteristic peaks of PPy[11] by the N—H stretching mode, C=C in-plane vibration of an aromatic ring, and C—H in-plane deformation vibration of an aromatic ring, respectively. This result also supports that pyrrole has been converted to PPy in the arachidic acid LB film by the role of $FeCl_3$.

The surface morphological features of the ferric arachidate LB film treated with HCl vapor and the arachidic acid/PPy composite LB film are shown in Figure 6. The LB film containing $FeCl_3$ only [Fig. 6(a)] does not have any specific morphological fea-

tures, while the arachidic acid/PPy composite LB film [Fig. 6(b)] has many small granules of PPy, which has been formed at the location of $FeCl_3$.

The effect of the exposure temperature on the composite film thickness is shown in Figure 7. The average thickness of the composite films prepared at 0, 25, and 50°C, respectively, by exposing 19 layers of arachidic acid LB film to pyrrole vapor was 1525,
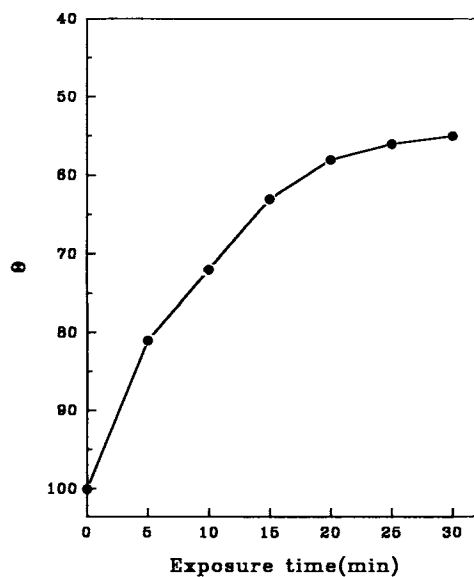
Figure 11   Surface wettability of arachidic acid/PPy composite films as a function of exposure time to pyrrole vapor.

1625, and 1710 Å. The samples prepared at lower exposure temperatures have more uniform thickness as shown in Figure 7. This might be due to the slow diffusion and polymerization rate of pyrrole in the arachidic acid LB film at lower exposure temperatures.

Figure 8 shows the effect of the exposure temperature on the morphology of the composite films. It is obvious that the composite films prepared at 0°C exhibited much more homogeneous distribution of small PPy granules within the matrix LB films than those prepared at a higher temperature (50°C).

From the current(I)–voltage(V) characteristics, the effect of the exposure temperature to pyrrole vapor on the in-plain conductivity and the transverse conductivity of the arachidic acid/PPy composite films were investigated and the results are presented in Figure 9. The in-plain conductivity was in the range of 10^{-3}–10^{-2}S/cm and the transverse conductivity was about 10^{-6}S/cm. Thus, the conductivity anisotropy is about 10^3. The conductivity increases with the decrease of the exposure temperature to pyrrole vapor. It was considered that the high exposure temperature might initiate side reactions and also result in less uniform film formation, as shown in Figure 8, followed by the resultant low conductivity. Figure 10 shows the stability of the composite films on the exposure to ambient air for 20 days. The conductivity decreases less than 1 order of magnitude even after 20 days' exposure. It was reported that carbonium ion structures of PPy are principally reactive with respect to oxygen and water, resulting in shortening the conjugation length.[12] But it is supposed that in this composite of LB films the matrix arachidic acid film serves as a barrier to oxygen and water and, thus, the composite film maintains a stable electrical property.

The surface property of LB films was estimated from surface wettability. The surface of ferric arachidate films showed the hydrophilic and hydrophobic property, alternately depending on the number of layers. The contact angle (θ) of the 18th layer with water drop was 27°, whereas that of the 19th layer was 100°. In Figure 11, the θ value for the 19th layer was plotted as a function of exposure time to pyrrole vapor at 25°C. On exposing to pyrrole vapor, the contact angle has been changed from 100° to 55°, which implies that the hydrophobic surface of the odd number layer becomes more hydrophilic by the formation of PPy in the ferric arachidate LB film.

CONCLUSIONS

Electrically conducting arachidic acid/PPy composite films can be prepared by exposing the preformed arachidic acid LB films containing $FeCl_3$ to pyrrole vapor.

The in-plain conductivity is in the range of 10^{-3}–10^{-2}S/cm, whereas the transverse conductivity is about 10^{-6} S/cm. The conductivity anisotropy of these composite films is about 10^3. From the electrical conductivity measurement, it is clear that the conductivity increases with a decrease of the exposure temperature. Also, the composite films prepared at lower exposure temperature to pyrrole vapor exhibited much more homogeneous distribution of small PPy granules within the matrix LB films. The conductivity decreases less than 1 order of magnitude even after 20 days' exposure to air.

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