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Preparation and characterization of Langmuir–Blodgett films of polyemeraldine base

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It is shown that transferable Langmuir monolayers can be formed at the air–water interface by dissolving polyemeraldine base in a solution of *N*-methyl-2-pyrrolidinone and $CHCl_3$. The Langmuir–Blodgett (LB) films of polyemeraldine base have been deposited on quartz substrates. These LB films have been characterized using u.v.–visible and *FT*i.r. techniques, respectively. It is seen that annealing of LB films of polyemeraldine base results in the modification of their optical properties. Copyright © 1996 Elsevier Science Ltd.

(Keywords: emeraldine base; polyaniline, NMP)

INTRODUCTION

The Langmuir–Blodgett (LB) technique has received considerable attention in recent years because it has been considered to be the best available method for the preparation of ultra-thin organic films with well-defined molecular structures[1,2]. A number of molecules with cylindrically shaped surface-active molecules possessing amphiphilicity such as fatty acids and fatty acid salts have been deposited on various substrates[3]. There have been a number of reports on non-polar macromolecules such as fullerenes[4] and metallophthalocyanines[5] being deposited by this method. There has been an increased interest towards the preparation of conducting polymer LB layers on to desired substrates[6]. LB films based on conducting polymers are attractive candidates for a variety of applications such as biosensors[7], ion sensors[8], integrated optics[9] and molecular electronic devices[10].

Conducting polyaniline has recently aroused much interest[11,12]. The reversible redox chemistry, high charge capacity, good environmental stability and electrochemical properties have led to many applications of polymers[13]. Polyaniline films can be fabricated by solution casting, electrochemical and dip-coating techniques. However, the nanoscale manipulation of polyemeraldine base for the fabrication of well-ordered thin films in large areas has been attempted only by a few researchers[14]. The LB films of polyemeraldine base have been deposited by incorporating a fatty acid in the aniline molecule, and the resulting anisotropic conductivity has been shown to arise from the alternating layers of conducting polymers and insulating polymeric layers[15]. The deposition of both quasi-ordered and ordered layers of polyaniline have recently been reported by Ram *et al.*[16] and Agbor *et al.*[17], respectively. A recent study conducted has unravelled the high-level molecular compatibilities of the polyion complex of sulfonated polyaniline and stearoylaniline films.

In the present paper, we report detailed studies on the preparation of Langmuir monolayers of emeraldine base. Further, systematic investigations pertaining to the characterization of mono/multilayers of emeraldine base have been carried out by u.v.–visible and *FT*i.r. techniques. The effect of annealing on the stability of the films of polyemeraldine base has also been reported.

EXPERIMENTAL

The emeraldine base form of polyaniline was chemically synthesized by oxidative polymerization of aniline using ammonium perdisulfate ($(NH_4)_2S_2O_8$) under controlled conditions[18,19]. The dark-green precipitate was filtered and subsequently washed with methanol and dried over P_2O_5. The green powder thus obtained is an emeraldine salt. The emeraldine salt thus obtained was subsequently treated in turn with aqueous ammonia, distilled water and acetone, and then vacuum dried for about 24 h to obtain the deprotonated form of polyaniline (emeraldine base). A solution of polyaniline for obtaining LB films was prepared by varying the percentage (30, 40, 50, 60, 80 and 100%) of $CHCl_3$ in *N*-methyl-2-pyrrolidine (NMP). The emeraldine base (0.1 mg) dissolved in different solvents (comprising $CHCl_3$ and NMP) was sonicated for about 30 min for each concentration. The resulting solutions were filtered with a solvent-resistant filter (0.5 μm) before use. The conducting polymer solution was spread uniformly on the water surface without any visible sign of aggregation.

LB film deposition was carried out using a Joyce–Loebl LB tough (model 4). The pressure–area isotherms of polyaniline obtained at different concentrations of NMP and $CHCl_3$ were performed at a barrier

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compression speed of 0.5 cm min^{-1} during the desired temperature range (9.2–40°C). The LB films of polyaniline were deposited at a surface tension of 25 mN m^{-1} and a barrier speed of 0.5 cm min^{-1}. Deionized water from a Millipore (model RTS-10) water purification system was used to fill the Langmuir trough, and the pH of the water was maintained at 7. The speed of the dipping head was maintained at 3 mm min^{-1}, and the temperature of the subphase was kept at 22°C by circulating the water in the trough using a refrigerated recirculator (BioRad Model E4870). The LB films were deposited on quartz plates. The spectroscopic measurements were carried out using u.v.–visible (Shimadzu 160 A) and *FT*i.r. (Nicolet 510 P) techniques.

RESULTS AND DISCUSSION

Figure 1a shows the pressure (π)–area (A) isotherm obtained at 22°C for emeraldine base when it is dissolved in $CHCl_3$. The liquid phases L_1 and L_2 are clearly visible in this pressure–area isotherm. It may be seen that these liquid phases (L_1 and L_2) are pronounced for molecular areas of 10 and 8 Å^2, respectively. The solid phase transition (*Figure 1a*) can be clearly seen to occur at the molecular area of 6.5 Å^2. The compressibility values at the L_1 and L_2 phases have been estimated to lie between 0.004 to 0.016, whereas the compressibility of the solid phase has been estimated to lie between 0.0005 and 0.001. *Figure 1b* exhibits the pressure–area isotherm obtained at 22°C for polyaniline dissolved in a mixture of NMP and $CHCl_3$. The liquid–gas (LG) condensation begins at about the molecular area of 36 Å^2. Interestingly, it can be seen that there is only one liquid phase (L_2) present in *Figure 1b*. The nature of the pressure–area isotherm (*Figure 1b*) obtained for the polyemeraldine base is similar to that reported for poly-2-decyloxyaniline[20]. It appears that solid phase condensation perhaps occurs at a surface pressure of 25 mN m^{-1} around the molecular area of 16 Å^2. The average area occupied per molecule of the polyemeraldine base has been estimated from the pressure–area isotherm by extrapolating the steepest region before the onset of the transition. However, it may be remarked that we do not fully understand at this stage the observed small change in the slope (*Figure 1b*) between the L_2 to S phases that may perhaps be due to the onset of a second-order phase transition.

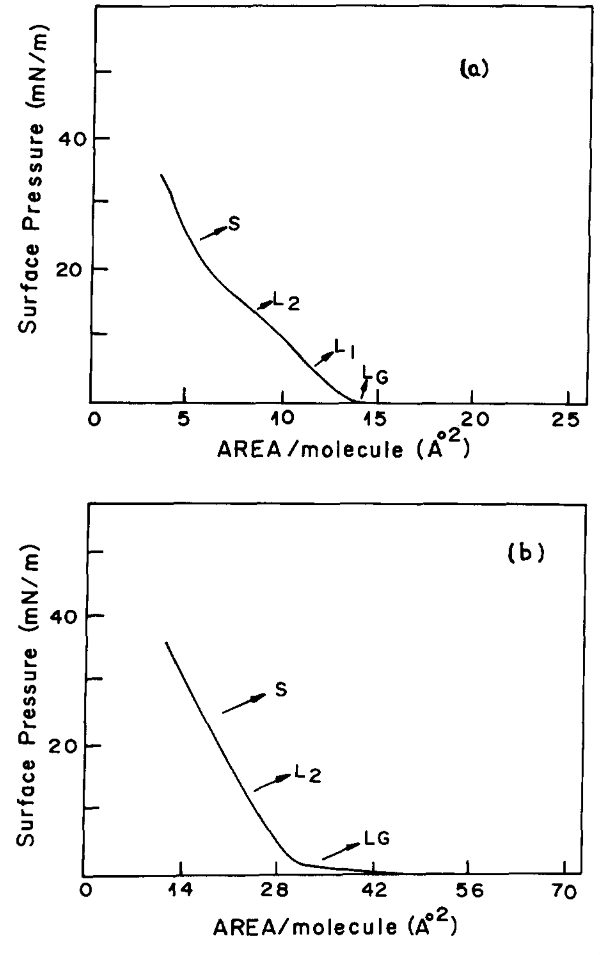

Figure 1 (a) Pressure–area isotherm of polyemeraldine base at 22°C when polyaniline is dissolved in $CHCl_3$. (b) Pressure–area isotherm of polyemeraldine base when polyaniline is dissolved in a mixture of 40% NMP and 60% $CHCl_3$

Figure 2a shows the plot of the molecular area of the solid phase of polyaniline obtained at a pressure of 25 mN m^{-1} as a function of NMP containing varying percentages of $CHCl_3$. Assuming the area per molecule of NMP is negligible, the area per molecule of the emeraldine base repeat unit at the solid phase is 16 Å^2. The limiting area of the LB films of polyaniline has been found to be in the range of 12–15 Å^2 per molecule. The minimum area is obtained when the emeraldine base is dispersed from a solution comprising 40% NMP and 60% $CHCl_3$ on the surface of the trough containing the deionized water. The ratio of NMP to $CHCl_3$ for the various solutions has been kept constant to eliminate any effects that may arise due to the solvent during LB film deposition. With a view to investigate the thermal stability of Langmuir monolayers of emeraldine base, pressure–area isotherms have been obtained covering a wide range of temperatures from 9.2 to 40°C when the emeraldine base is dissolved in a solvent comprising

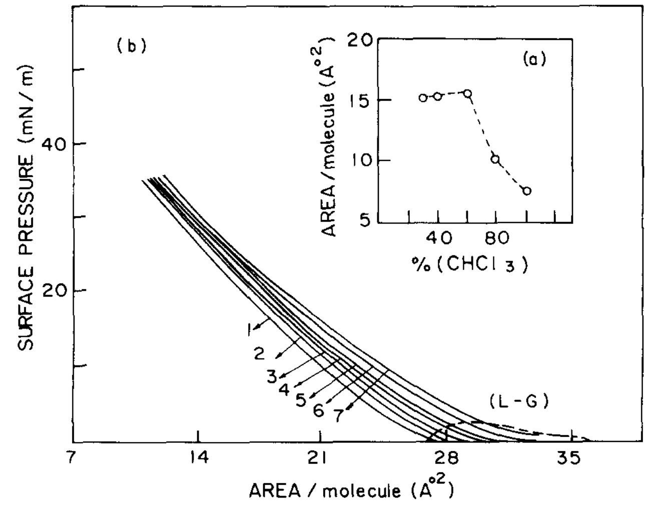

Figure 2 (a) Variation of area per molecule of polyemeraldine base as a function of NMP containing varying percentages of $CHCl_3$ at a pressure of 25 mN m^{-1}. (b) Variation of the pressure–area isotherm as a function of temperature at 9.2°C (curve 1), 15°C (curve 2), 22°C (curve 3), 26°C (curve 4), 29°C (curve 5), 34°C (curve 6) and 40°C (curve 7)

of 40% NMP and 60% $CHCl_3$ (*Figure 2b*). It can be seen that LG phase transition occurs when the area per molecule of emeraldine base changes from 27 to 35 Å^2. It is noticed that the solid condensation area changes from 15.91 to 17.0 Å^2 as the temperature varies from 9.2 to 40°C. In addition, it can be seen that the nature of the various pressure–area isotherms remains the same, indicating the thermal stability of Langmuir monolayers of the polyemeraldine base on the surface of water.

Figure 3a (curve 1) shows the variation of surface pressure of the solid phase obtained as a function of temperature. As the temperature of the subphase increases from 9.2 to 40°C, the surface pressure increases from 27.5 to 28.2 mN m^{-1}. Curve 2 in *Figure 3a* exhibits the observed variation in the molecular area obtained for a solid phase as a function of temperature (9.2–40°C) at a pressure of 25 mN m^{-1}. It can be seen that there is no significant change in the molecular area of the solid phase with an increase in temperature. *Figure 3b* exhibits the variation in the molecular area displaced from the trough against the number of strokes after the LB film has been deposited on a quartz substrate. It is significant to note that up to about 12 monolayers, transferred from the trough, the molecular area shows a change of about 1.5 cm^{-2}. However, after the transfer of about 24 monolayers from the trough, the mode of deposition is seen to change from the Y to X type[16].

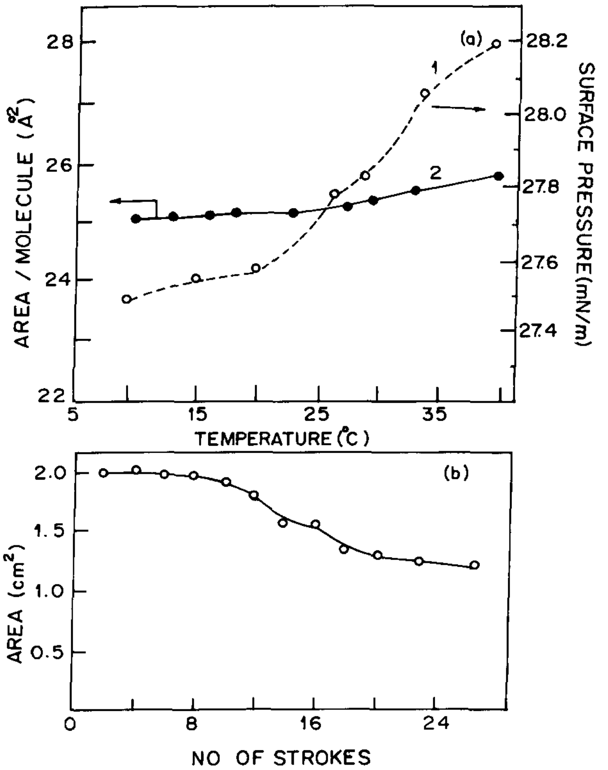

Figure 3 (a) Variation of the surface pressure of the solid phase as a function of temperature (curve 1) and variation of the molecular area in the solid phase at a pressure of 25 nM m^{-1} as a function of temperature. (b) Area displaced from the LB trough as a function of deposition strokes; area of the ITO glass substrate used for deposition of LB films is 2 cm^2

Figure 4 shows the *FT*i.r. spectra of LB films of polyemeraldine base obtained for 20 (curve 1), 24 (curve 2), 32 (curve 3) and 40 (curve 4) monolayers. The peaks seen at 1780, 1715, 1568, 1270, 1032, 925,800, 700, 604 and 531 cm^{-1}, are characteristic of polyemeraldine base. The 1715 and 1590 cm^{-1} peaks have been attributed to the aromatic C=N bond (quinoid) of the polyemeraldine base. The strong band seen at 1325 cm^{-1} can be assigned to the combination of several stretching and bending vibrations emanating from the C=N bonds. The peak at 874 cm^{-1} can be understood to arise from the C=H stretching of emeraldine base[21]. As in the case of various other LB films, the intensities of the various peaks in the respective *FT*i.r. spectra show a distinct decrease with an increase in the number of monolayers.

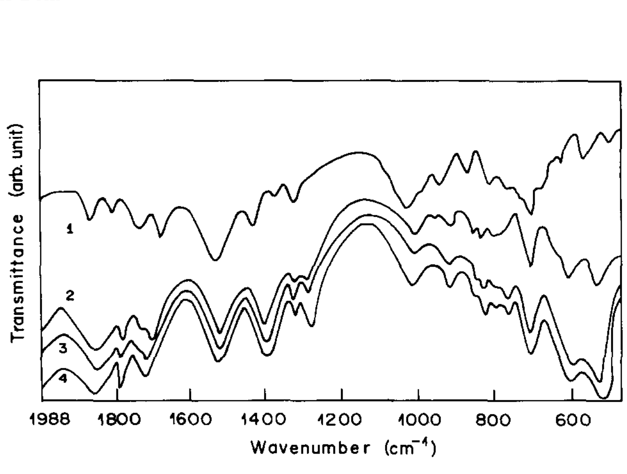

Figure 4 *FT*i.r. spectra obtained as a function of the number of monolayers of polyaniline LB films: curve 1, 20 monolayers; curve 2, 24 monolayers; curve 3, 32 monolayers; curve 4, 40 monolayers

Figure 5 is the u.v.–visible spectrum of polyaniline obtained as a function of monolayers for freshly prepared LB films prepared on quartz substrates. The LB films of polyemeraldine base show two sharp absorption peaks at about 370 nm (3.356 eV) and 619 nm (2.04 eV)[22,23]. The peak seen at 370 nm can be attributed to the π–π* transition centred on the benzenoid ring[17], and the peak at 610 nm can be understood to arise from the n–π* transition[24]. It is interesting to see that the intensity of the broad band (1000–1300 nm) shows a distinct increase with each additional monolayer. To examine the effect of

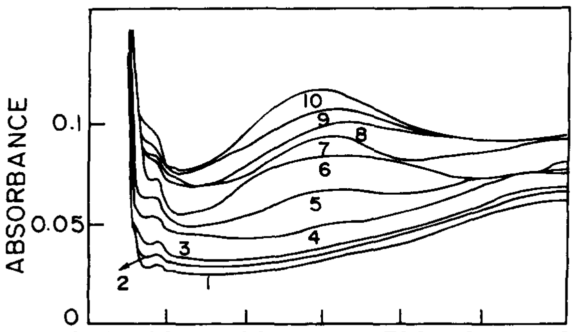

Figure 5 Variation of the u.v.–visible absorption of polyemeraldine LB films as a function of the number of monolayers: curve 1, two monolayers; curve 2, four monolayers; curve 3, six monolayers; curve 4, eight monolayers; curve 5, 10 monolayers; curve 6, 12 monolayers; curve 7, 14 monolayers; curve 8, 16 monolayers; curve 9, 18 monolayers; curve 10, 20 monolayers

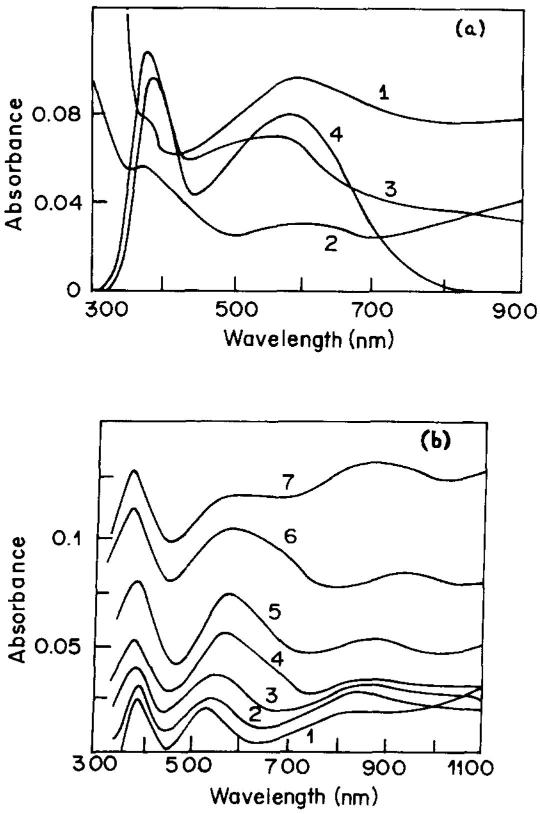

Figure 6 (a) Variation of the u.v.–visible spectrum of 20 monolayers of LB films of polymeraldine base as a function of annealing (50°C) time: curve 1, freshly prepared films; curve 2, 10 h; curve 3, 24 h; curve 4, 48 h. (b) U.v.–visible absorption spectra of doped LB films of polyaniline in 1 M HCl as a function of monolayers; curves 1–7 are for 4, 8, 16, 20, 28, 32 and 41 monolayers, respectively

annealing, u.v.–visible studies of an LB film (20 monolayers) of polyemeraldine base for various durations of time have been conducted. *Figure 6a* (curve 1) is the u.v.–visible spectrum of a freshly prepared LB film (20 monolayers) of the polyemeraldine base. Curves 2, 3 and 4 (*Figure 6*) are the u.v.–visible spectra obtained for LB films of polyemeraldine base annealed at 50°C for 12, 24 and 48 h, respectively. It can be seen that the 370 nm and 610 nm peaks appear to become sharper with an increased annealing time in excess of about 10 h. This result may perhaps be attributed to the release of entrapped solvent from the polyemeraldine base film. The ordered structure of the polyaniline films has earlier been observed as a consequence of doping with HCl (1 M). *Figure 6b* shows the u.v.–visible absorption spectra obtained as a function of annealed (4 h) monolayers of emeraldine base when these are treated with HCl (1 M) for about 10–15 min. The protonic acid doping in the emeraldine base results in the shift of the Fermi level resulting from the migration of electrons from the valence band into the conduction band. The maximum doping in the emeraldine base is about 50% with protonic acid doping, whereas the dications are formed near the quinoid ring of the emeraldine base LB films. The intensities of absorption bands seen at 400, 530 and 850 nm have been found to increase uniformly with the increase in the number of monolayers. The observed increase in the optical intensity of the 850 nm peak is perhaps due to the presence of polaron bands. It is significant to note that the intensity of the n–π^* transition (370–400 nm) is sharper than other peaks, as has been observed in the case of polyaniline films prepared by other techniques.

CONCLUSIONS

It has been demonstrated that stable Langmuir monolayers of polyemeraldine base can be formed by dissolving polyemeraldine base in a solution comprising NMP and $CHCl_3$. It has also been revealed that monolayers of polyemeraldine base are thermally stable over a wide range of temperatures (19.2–40°C). The area per molecule of the emeraldine base repeat unit in the solid phase has been found to be 16 $Å^2$. It is seen that annealing of LB films of polyemeraldine base results in the modification of their optical properties. In order to further verify this result, detailed investigations with regard to the structure of LB films of polyemeraldine base using scanning electron microscopy, X-ray diffraction and atomic force microscopy (AFM) techniques are presently in progress.

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