Electrochemistry of polyaniline Langmuir–Blodgett films

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Abstract

Langmuir–Blodgett (LB) manipulation of polyaniline has been variously employed to obtain organized assemblies for use in molecule-based electronic devices. However, the electrochemical characteristics of polyaniline LB films which have a direct implication on the proposed device applications have not been given much attention. We report here, electrochemical characterization of multilayer LB films of polyaniline prepared by employing *N*-methylpyrrolidone as the processing solvent. The films have been transferred onto a variety of substrates such as quartz, platinum, platinum sputtered on quartz, and conducting tin oxide on glass. The electrochemistry of polyaniline LB films has been studied using cyclic voltammetry coupled with a quartz crystal microbalance (QCM). Cyclic voltammograms were obtained for films transferred at different surface pressures, for films containing different number of layers. The electrochemical characteristics of LB multilayers were compared with those of electrochemically deposited films and were used to infer the packing behaviour of polymer chains in the LB film structure. It was found that multilayer LB films are electroactive but the kinetics of counter ion transport in these films is slower than that observed in electrochemically deposited films. The multilayer LB films also show poor electrochromic switching behaviour.

Keywords: Electrochemistry; LB films; Molecular electronics; Polyaniline

1. Introduction

Organic conductors are materials with potential for molecular electronics. Conducting polymers are more attractive than charge-transfer complexes because of their demonstrated device applications [1]. Among conducting polymers, polyaniline is of special interest, primarily due to its higher environmental stability and ease of preparation. Organization of conducting polymers in specific arrangements that would give the desired material properties is getting increasing attention, as this kind of organization is important for the development of many novel molecule-based electronic devices. In this regard, Langmuir–Blodgett (LB) manipulation of conducting polymers seems promising, as it usually results in ultra thin films with known thickness and molecular orientation [2,3]. The poor processibility (insolubility in common organic solvents used in the LB technique) and the lack of amphiphilicity are two important factors that have restricted the LB deposition of conducting polymers. However, in recent times, LB films of conducting polymers have been obtained with various molecular engineering approaches. With reference to polyaniline, these include the derivatization of the polymer with long alkyl chains [4,5], doping with an amphiphilic dopant [6] and co-LB deposition along with typical film forming materials [1,7,8]. LB film deposition of parent polyaniline employing *N*-methylpyrrolidone (NMP)/chloroform mixture [9,10] or pure NMP [11] as processing solvent has also been reported. While most studies report spectroscopic characterization and there is a recent report on AFM characterization [12], the electrochemical characteristics of polyaniline multilayer LB films have not been given much attention [10,13,14]. We felt that such studies are of direct relevance to the performance of electronic devices based on polyaniline LB films. In the present report, we describe a detailed investigation of the electrochemistry of polyaniline LB films. LB films of polyaniline were made with NMP as the processing solvent [11]. The electrochemical behaviour of multilayer films have been studied by cyclic voltammetry coupled with a quartz crystal microbalance. The results have been used to
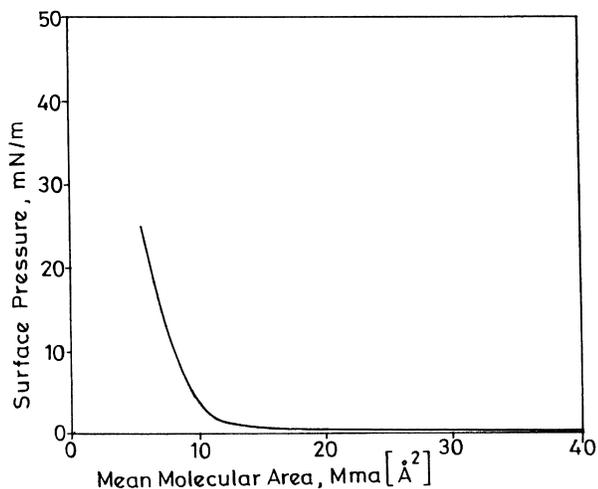
Fig. 1. π-A isotherm of polyaniline monolayer at subphase temperature of 21°C and pH of 4.0. Compression speed 3 mm/min.

draw some conclusions about the packing arrangement of polymer chains in the LB film structure.

2. Experimental

Polyaniline (EB) was prepared chemically employing the method reported by MacDiarmid et al. [15]. NMP (from Sisco Research Labs., purity 99.5%) was used as the processing solvent. Control experiments were carried out by spreading the solvent on the surface of water and subsequent compression to confirm the absence of any surface active impurities. Deionized and Millipore-filtered water (resistivity better than 18 Mohm cm) was used for making the subphase of pH equal to 5.8. The spreading solution was obtained by dissolving a mixture of polyaniline and acetic
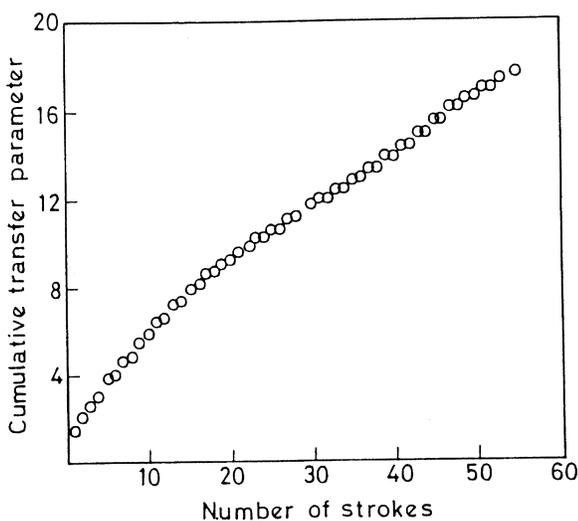

Fig. 2. A plot of the sum of transfer ratios (CTP) vs. the number of layers of polyaniline LB films transferred on platinum plate. Transfers were carried out at a surface pressure of 18 mN m^{-1}.

acid (10:1 w/w ratio) in NMP in an ultrasonic bath for 1 h. The undissolved particles were filtered off prior to use. The weight fraction of undissolved particles is about 40%. We have corrected for the amount of undissolved particles while calculating the mean molecular area. Freshly prepared spreading solution was used within 10 days. The typical concentration is about 0.08 mg/ml. Mean molecular area has been calculated on the basis of molecular weight of polyaniline repeat unit which consists of a benzenoid unit, a quinoid unit and an imine unit (molecular formula: $C_{24}H_{18}N_{14}$; formula weight: 362). Surface pressure-mean molecular area isotherms and multilayer LB depositions were obtained with a KSV-3000 instrument kept in a clean room. Quartz, platinum plate and platinum sputtered on quartz were used as substrates. Quartz substrates were cleaned by treating with hydrogen peroxide-ammonia mixture at 70°C followed by ultrasonic cleaning with organic solvents and were kept in deionized water until use. Platinum plates were cleaned electrochemically in 0.5 M H_2SO_4 using the galvanostatic mode by passing anodic and cathodic currents of 10 mA cm^{-2} for 20 min. UV-vis spectra were obtained with a Shimadzu-160A spectrophotometer. Electrochemical measurements were done with an EG&G PARC 273 potentiostat using a cell arrangement as follows. The LB film deposited on platinum plate was held horizontally and a Teflon coated silicone 'O' ring was placed on the film to define the electrode area (area = 0.442 cm^2). A drop of 0.5 M sulfuric acid was pipetted in the area defined by the 'O' ring and the platinum plate was connected to the working electrode lead. Platinum wire and saturated calomel electrode were used as counter and reference electrodes respectively (see [11] for a schematic figure). The potential was scanned between -200 and 800 mV at a scan rate of 50 mV s^{-1}. Quartz crystal microbalance (QCM) measurements were carried out with a Seiko EG & G quartz crystal analyzer, model QCA 917. AT-cut quartz crystals (9 MHz, 8.88 MHz in solution, size = $0.8 \times 0.8 \times 0.02$ cm^3) sputtered with platinum (area = 0.193 cm^2) with an underlayer of titanium were also used as substrate for the multilayer LB deposition. One of the faces of the crystal was exposed to the electrolyte by fixing the LB film deposited crystal in a well type Teflon holder using a viton 'O' ring. The face exposed to the electrolyte also served as the working electrode. The sensitivity of the crystal was calculated to be 5.604 ng/Hz per cm^2, based on the Sauerbrey equation [16]. Analog data were recorded with a Linseis 16100 II X-Y recorder.

3. Results and discussion

A typical surface pressure-mean molecular area isotherm of polyaniline monolayer obtained by employing NMP as processing solvent is shown in Fig. 1. A stable and close packed monolayer with a limiting mean molecular area of 7.8 ± 0.2 Å^2 was obtained. The monolayers were trans-
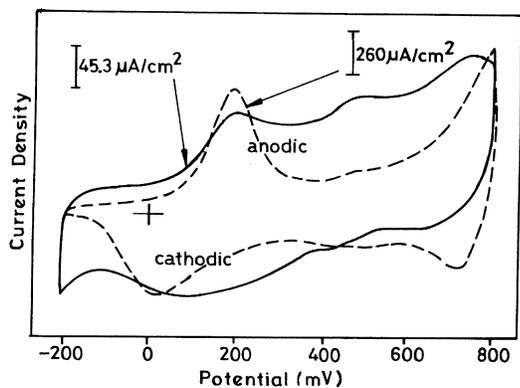
Fig. 3. Cyclic voltammograms of (a) LB film of polyaniline (25 layers) deposited on platinum plate and (b) an electrochemically deposited polyaniline film recorded in 0.5 M H_2SO_4 (scan rate=50 mV s^{-1}).

ferred onto different substrates at a constant surface pressure of 18 mN m^{-1} by the vertical dipping method (dipping speed = 2 mm min^{-1}) at subphase pH of 4.0 and a temperature of 20°C. Deposition was mostly of Z-type with poor transfer during the first few dipping strokes. Transfer onto quartz substrates was characterized by near unity transfer ratios (TR) till about 50 layers. Uniform transfer has also been inferred from the linear increase of absorption (in UV-vis spectra) with the number of layers [11]. However, with platinum as substrate, the transfer became relatively poor (lower TR) beyond 25 layers. A plot of the sum of transfer ratios vs. the layer number is shown in Fig. 2. In order to compare the transfer efficiency with layer thickness, we have used a parameter which we call the cumulative transfer parameter (CTP), which has been defined to be the sum of transfer ratios for the given number of strokes. The ideal
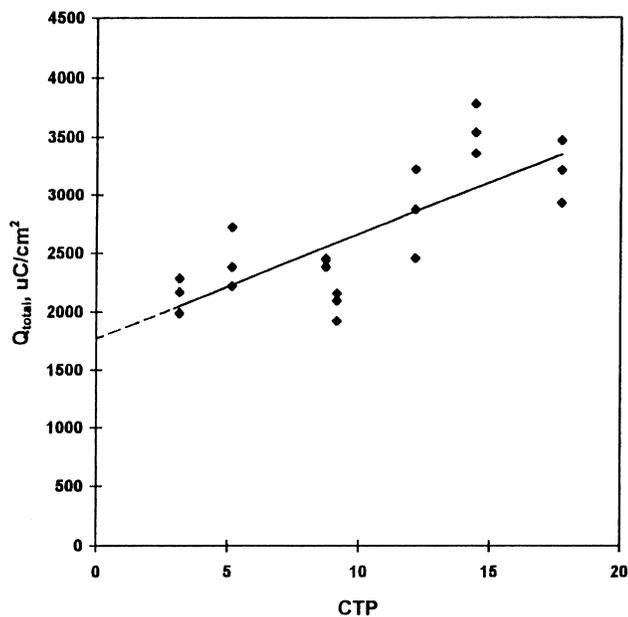

Fig. 4. A plot of total redox charge per unit area, Q_{total} vs. CTP in multilayer polyaniline LB films.

cumulative transfer parameter for a perfect Y-type deposition should be equal to the total number of both up and down strokes (n), while for a perfect Z-type deposition, it should be nearly half the total number of strokes (n + 1)/2. This parameter is a measure of the quantity of material transferred for a given number of strokes.

The electrochemical characteristics of polyaniline LB films can be deduced from the CV measurements. In our earlier study [11], we have shown that the total redox charge per unit area, Q_{total}, which was calculated from I–V response of multilayer polyaniline LB films (17 layers) transferred at different surface pressures (8, 13, 18, 25 and 30 mN m^{-1}), was different. The redox charge per CTP associated with the film transferred in the liquid region was found to be higher than that observed with the films transferred in the solid region of the isotherm. In the present study, all the films were transferred at a constant surface pressure of 18 mN m^{-1}. The cyclic voltammograms of a polyaniline LB film (25 layers) deposited on a platinum plate (a) and an electrochemically deposited film (b) are shown in Fig. 3. The features are indicative of the typical redox behaviour of polyaniline. However, the peaks of the LB films are broader compared to those of electrochemically prepared polyaniline thin films. The peak currents increase linearly with the sweep rate (from 25 to 1000 mV s^{-1}), confirming that the currents correspond to redox processes involving surface confined electroactive species [10]. The total current is the sum of faradaic and charging currents. It appears that the charging currents for LB films are larger than those for electrochemically deposited films. The voltammetric behaviour of LB films with different numbers of layers was also studied. Irrespective of the number of layers, all the multilayer LB films ranging in thickness from seven to 55 layers exhibited CVs of similar shape. The total charge, Q_{total}, involved in the anodic and cathodic reaction of polyaniline has been calculated by integration of the I–V response. Q_{total} was found to increase with increasing number of layers, as shown in Fig. 4. The intercept on the y-axis may correspond to the charging process which seems to be dominant in these CVs as compared to electrochemically prepared films. Since there is a significant charging contribution to the CV, it is necessary to correct the total charge for this contribution. If we assume that the capacitive charging processes correspond to the metal/polymer interface and the polymer/solution interface, then this contribution should be independent of the number of LB layers transferred, since each new deposition destroys the old polymer/solution interface and creates an identical polymer/solution interface. If we assume that the intercept on the y-axis represents this charge, Q_c, it can be subtracted from the total charge to obtain the faradaic charge, $Q_f = Q_{total} - Q_c$. A plot of this corrected charge per layer, Q_f/CTP vs. cumulative transfer parameter, CTP, is shown in Fig. 5. For comparison, Q_{total}/CTP, the total redox charge per layer is also shown. If the whole film is uniformly electroactive, the faradaic charge per layer should be independent of the number of layers in
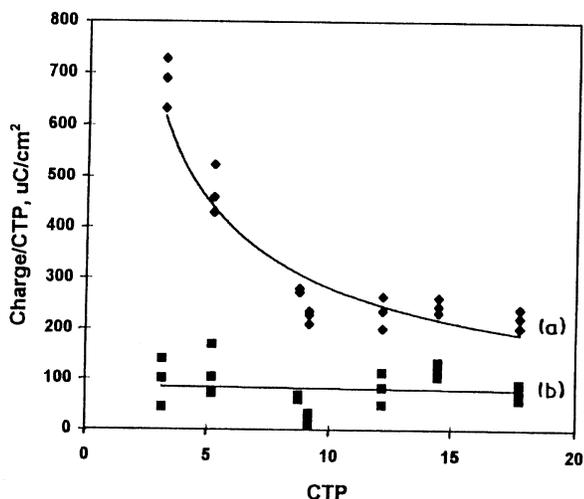
Fig. 5. Plots of (a) the total redox charge per layer, Q_{total}/CTP and (b) the corrected faradaic charge per layer, Q_f/CTP vs. CTP for films transferred onto platinum.

Fig. 7. A plot of the anion mass incorporated during the anodic scan (from −200 mV to +600 mV) vs. the cumulative transfer parameter, CTP, of polyaniline LB films.

the LB film. The results in Fig. 5 show that it is indeed so and the faradaic charge per layer is 87 μC/cm²/CTP. However, the total charge per layer, Q_{total}/CTP, decreases exponentially with increasing CTP, tending to a constant value at high CTP. This can be expected if there is a constant contribution from the charging process which will become relatively smaller with increasing CTP.

During electrochemical scanning, the redox charge is quantitatively related to the inclusion and expulsion of anions (counter ions) into and from the film. It is known that in the case of the electrochemically prepared polyaniline thin films, the total redox charge increases with the film thickness, independent of the methods of preparation of the polymer [17]. The electrochemically prepared films are known to be porous in nature and thereby facilitate the movement of anions through the film during the potential scanning process [18]. This results in sharp redox peaks in
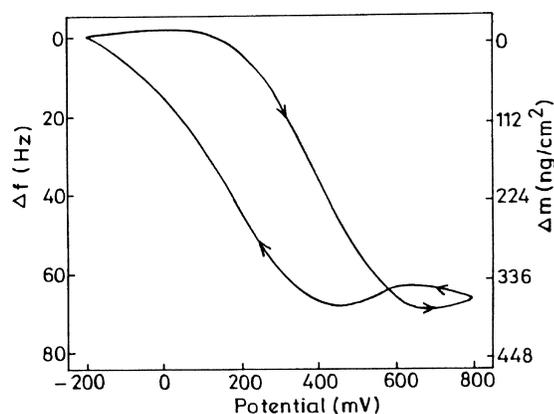
CVs and a linear increase of total redox charge with the increasing film thickness. However, in the case of LB films, during the electrochemical cycling, the close packed polymer chains in the LB film may impose some restriction on the movement of anions. We have used the quartz crystal micro balance to follow the mass changes accompanying potential cycling of the polyaniline LB films. An increase in mass at the crystal surface results in a decrease in the resonant frequency of the crystal [16]. Fig. 6 shows the resonant frequency profile of a 33-layer polyaniline LB film deposited on the QCM crystal during the potentiodynamic scan between −200 to +800 mV. The resonant frequency decreases with increasing anodic potential. The corresponding increase in mass is associated with the inclusion of anions which are required to compensate for the positive charge created on the polymer and maintain electro-neutrality. This is in agreement with similar observations with electrochemically prepared polyaniline films [18,19]. During the cathodic scan, there is an expulsion of the anions and a corresponding decrease in mass and increase in resonant frequency. The number of anions included/expelled from the film during the scan must be proportional to the amount of electroactive polymer on the surface. This is confirmed by the observation that the mass increase due to anion inclusion increased linearly with the cumulative transfer parameter, as shown in Fig. 7. It is consistent with the observed increase in the redox charge with increasing CTP (Fig. 4). This confirms that the LB multilayers are uniformly electroactive. The mass of anions exchanged with the film during a potential scan is estimated to be about 17.8 ng cm^{-2} CTP^{-1} for platinum. We have attempted to compare the mass of anions incorporated in the polymer during the anodic potential scan for electrochemically prepared films and LB films. The mass of electrochemically deposited films was determined in situ by noting the drop in resonant frequency at −0.2 V at various times of polymerization. The mass of LB films was obtained from the CTP and the mean molecular area at the surface at which

Fig. 6. The change in resonant frequency(Δf) and mass(Δm) as a function of potential for polyaniline films transferred onto platinum-coated quartz crystal surfaces.
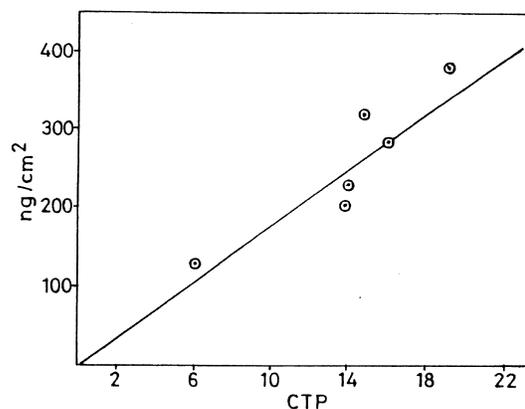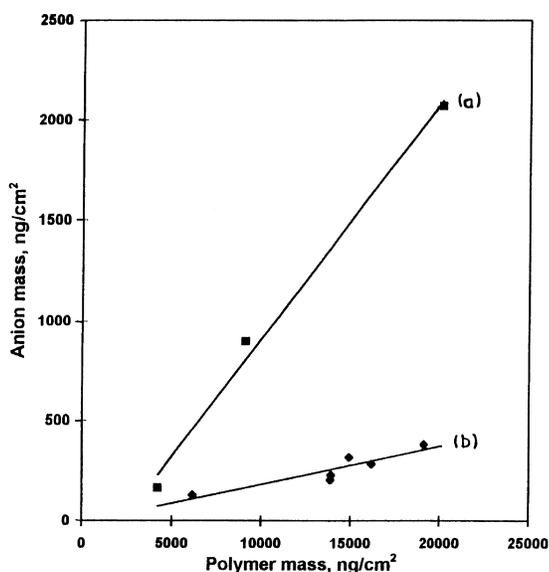
Fig. 8. A plot of the anion mass incorporated during the anodic scan as a function of the polymer mass for (a) electrochemically synthesized and (b) LB films of polyaniline.

the film was transferred. Thus,

Polymer mass $= (362 \times \text{CTP})/(L \times \text{mean molecular area})$

where 362 is the molecular weight of the repeat unit used for mean molecular area calculation and L is the Avogadro number. These films were subjected to cycling in the absence of the monomer and from the frequency-potential curves the mass of anions incorporated during the anodic scan was estimated. Fig. 8 shows a plot of the anion mass vs. the corresponding polymer mass for both types of films. It is obvious that for a given polymer mass, the electrochemically synthesized film can take up a higher anionic mass than the LB film, almost five times as high. This is consistent with our observation that LB films of polyaniline are not as electroactive as the electrochemically synthesized ones. Due to the tighter packing in LB films, major portions of the polymer chains are unable to undergo the conformational changes necessary for electron transfer and ion binding.

Electrochemically prepared films are known to exhibit a clear reversible electrochromism on varying applied potential and this behaviour is associated with conformational changes of polymer. On scanning from −200 to 800 mV (Vs SCE), electrochemically prepared films undergo dramatic sequential color changes from transparent yellow–light green–green–blue–violet [15]. However, on varying the applied potential of LB films, significant color changes were not observed even with the thickest multilayer film (55 layers). The color turned from pale to dark. The poor electrochromism observed in the multilayer LB films might be a reflection of the conformational constraints introduced due to tight packing of the polymer in monolayers. This is in contrast to an earlier report [13], of a clear chromic

change, as normally seen with electrochemically prepared films, in LB film of a single polyaniline monolayer transferred on tin-oxide glass. The single polymeric LB monolayer transferred onto the substrate was shown to posses a number of pinholes and micro defects. The CV showed sharp redox peaks as seen for electrochemically synthesized films. The relatively poor packing of the monolayer polyaniline film leads to electrochemical behaviour similar to electrochemically synthesized films.

4. Conclusions

Langmuir–Blodgett films of polyaniline (EB) were prepared by employing N-methylpyrrolidone as the processing solvent. The electrochemical characteristics of polyaniline LB films were studied by cyclic voltammetric measurements. The total redox charges calculated from the I–V response are found to increase linearly with increasing number of layers. Measurements indicated that multi-layer polyaniline LB films exhibited slow redox kinetics (broad redox peaks) and also resulted in poor electrochromism, in comparison with electrochemically prepared thin films. Although like the electrochemically prepared film, the whole LB film is found to be electroactive, the closely packed polymer chains in the LB film structure impose restrictions on conformational changes and the movement of ions during the potential scan. Quartz crystal microbalance measurements indicate that the mass associated with anion inclusion during the anodic scan increases linearly with increasing numbers of layers, supporting the observation of increase in redox charge with increasing number of layers. These results on polyaniline LB films have direct implications on the use of these films in molecular devices.

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