Preparation of Langmuir−Blodgett Films of Soluble Polypyrrole

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Received May 1, 1997; Revised Manuscript Received December 2, 1997

ABSTRACT: Stable monolayers of soluble parent polypyrrole (Ppy) and mixed monolayers of cadmium stearate and Ppy were studied for the first time using surface pressure and surface potential isotherms. Ppy was obtained by chemical polymerization of the pyrrole monomer in the presence of dodecylbenzene sulfonic acid and characterized by ultraviolet−visible (UV−vis), Fourier transform infrared (FTIR), and elemental analysis techniques. Pure Ppy monolayers could only be transferred if optimized experimental conditions were employed, but mixed monolayers could be easily transferred in the form of Y-type Langmuir−Blodgett (LB) films, with a uniform layer-by-layer transfer according to UV−vis results. The FTIR spectrum indicated the presence of cadmium stearate along with Ppy. X-ray diffraction patterns showed the presence of cadmium stearate domains. The transferred LB films were characterized by electrical conductivity, cyclic voltammetry, and surface potential measurements.

1. Introduction

Langmuir−Blodgett (LB) processing of conducting polymers is of interest both for the exploitation of the electrical properties of these materials and for the molecular control provided by the LB technique. Using this method, molecules can be assembled in a required fashion, and the resulting thin films often possess defined molecular architectures and controllable thickness.[1,2] Thin films of polypyrrole (Ppy), in particular, are being considered as important functional components in different molecule-based devices, such as sensors, based on the redox property of these polymers,[3,4] and polymer-based LEDs as semitransparent anodes.[5] LB films of Ppy have been obtained in previous works by transferring the monolayer of substituted pyrrole followed by the electrochemical polymerization in the LB film structure.[6,7] Reports have also appeared on LB multilayers from Langmuir monolayers obtained by spreading amphiphilic Ppy derivatives at the air−water interface or obtained by chemical polymerization of parent pyrrole along with builders.[8−10] Another method of obtaining thin Ppy films, using LB templates of ferric stearate, has been employed by several researchers.[4,11,12] The LB processing of alkyl-substituted Ppy with amphiphilic counterions, obtained by electrochemical polymerization of the alkyl pyrrole monomer in the presence of a supporting electrolyte perfluorooctanoic acid, has also been reported.[13] The use of several distinct procedures point to the difficulties associated with the LB processing of the parent Ppy because of its poor solubility in common spreading solvents employed in LB experiments. The recent advent of dopant-induced processibility using amphiphilic dopants is extremely promising as it paves the way to dissolve the otherwise insoluble polymers in common organic solvents, such as chloroform, and thereby to obtain thin cast and LB films.[14] This dopant-induced processibility has been extensively − and successfully − used in the LB processing of parent polyaniline.[15,16]

In a recent work,[17] soluble parent pyrrole was obtained by chemical polymerization of the pyrrole monomer in the presence of ammonium persulfate as oxidant and dodecylbenzene sulfonic acid as the dopant. To our knowledge, there is no report on the LB manipulation of this soluble parent Ppy in the literature. In the present work, we report on the formation of stable monolayers of pure soluble Ppy and the composite monolayers containing cadmium stearate and Ppy. Monolayer characteristics were studied by surface pressure and surface potential isotherms. The composite monolayers could easily be transferred onto solid substrates and characterized.

2. Experimental Section

2.1 Synthesis and Characterization of Ppy. Stearic acid (99%) was purchased from Aldrich and used as received without further purification. Soluble Ppy was prepared by the method reported in ref 17 as follows: the pyrrole monomer (Riedel de Haen) was purified by distillation under reduced pressure and stored in a dark and cold place prior to use. Pyrrole (9.7 g, 150 mmol) and dodecylbenzene sulfonic acid (DBSA; 24.4 g, 75 mmol) were dissolved in distilled water by stirring with a magnetic stirrer at room temperature for 2 h. This solution was then placed in a low-temperature bath and 6.8 g (30 mmol) of ammonium persulfate (AR grade, 98%) dissolved in distilled water were added to the solution in a dropwise manner over a period of 2 h, with the bath temperature kept at 0 °C. The whole mixture was then stirred with a mechanical stirrer for 40 h at 0 °C. The reaction mixture turned dark green and became viscous with the progress of the reaction. The polymerization reaction was quenched by adding methanol to the reaction mixture. The separated dark-colored solid was filtered at the pump and thoroughly washed with distilled water (to remove excess oxidant), methanol, and acetone (to remove unreacted monomers and oligomers) and finally dried under dynamic vacuum for 24 h. The weight of the dark brown-colored powder thus

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S0024-9297(97)00606-2 CCC: $15.00

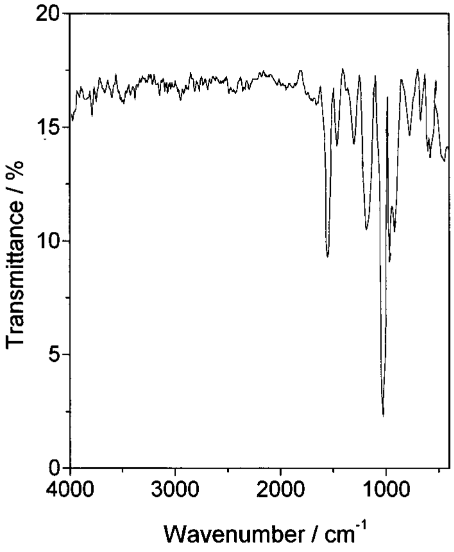

Figure 1. FTIR of bulk Ppy in the form of KBr pellet.

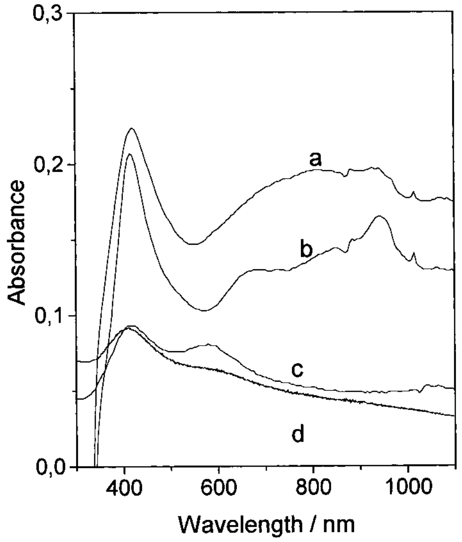

Figure 2. UV–vis spectra of (a) Ppy in *m*-cresol and chloroform solution in the presence of DBSA; (b) Ppy in *m*-cresol and chloroform solution; (c) composite LB film (27 layers) of Ppy and cadmium stearate; and (d) LB film of Ppy (13 layers).

obtained was ~3.0 g. The polymer sample was partially soluble in *m*-cresol upon ultrasonication for a few hours.

Before proceeding to the LB film preparation, Ppy was characterized by elemental analysis carried out with an Eager 200 CHNS analyzer, Fourier transform infrared spectroscopy (FTIR) with a BOMEM Michelson series instrument (transmission, resolution, 4.0 and scans, 32) and ^{13}C NMR spectroscopy (Varian Unity Plus-400). Solutions of Ppy were investigated by ultraviolet–visible spectrophotometry (UV–vis) with an Hitachi U200 spectrophotometer in the transmission mode.

From the elemental analysis (C, 68.5%; H, 7.4%; N, 9.2%; and S, 5.5%), the S/N ratio of the polymer sample was ~0.5, which agrees well with the value reported in the literature for the polymer with 25% doping of DBSA.[17] The presence of DBSA was also noticed in the solid-state ^{13}C NMR results obtained for the bulk polymer, indicating methylene (probably from DBSA) and aromatic (from Ppy and DBSA) carbons. However, results from FTIR obtained with a KBr pellet failed to confirm the presence of DBSA. As shown in Figure 1, there are clear absorption peaks for the Ppy, but there was no strong C–H absorption for the DBSA. Also, in the 4000–2000-cm^{-1} region there was no broad absorption band characteristic of a fully doped polymer. Similar FTIR results were obtained with a cast film made from the soluble portion of the polymer sample.

The contradictory results just discussed probably indicate that the polymer is only partially doped. Indeed, the UV–vis spectrum of the portion of the polymer sample soluble in the *m*-cresol–chloroform mixture (the spreading solvent in the LB experiment) exhibited broad absorption peaks at 415, 620, and 945 nm. This UV–vis spectrum, shown in Figure 2, indicates some degree of doping because of the absorption in the near-IR region, but it is different from that reported in ref 17; that is, a bipolaron absorption at 480 nm and a strong free carrier tail absorption in the near-IR region, characteristic of an entirely doped polymer with expanded chains. When the bulk Ppy reported here was treated with DBSA in a mixture containing *m*-cresol and chloroform, the UV–vis spectrum for the solution after filtration of undissolved particles exhibited an increase in the absorption in the long wavelength region, but still was not comparable to that of ref 17 (see Figure 2). Such differences are probably associated with the degree of doping and chain conformation.[18]

2.2 LB Film Preparation. The spreading solution for the LB experiments were obtained by dissolving Ppy in *m*-cresol (Merck, 99%) ultrasonically for 3 h followed by filtering the undissolved particles and diluting the mixture with chloroform (Merck, HPLC grade). The ratio of *m*-cresol and chloroform was 1:9. For obtaining composite LB films, the spreading solution was obtained by dissolving different amounts of stearic acid and Ppy in the mixture of *m*-cresol and chloroform. The spreading solution was greenish brown. Ultrapure water supplied by a Milli-RO coupled to a Milli-Q purification system from Millipore (resistivity 18.2 MW cm^{-1}) was used to prepare subphase solutions. In the case of pure Ppy monolayers, ultrapure water was used as the subphase. However, in the case of composite monolayers, the subphase comprised a solution of 4×10^{-4} M cadmium chloride (99.5%, Carlo Erba) whose pH was maintained at ~6.0 by adding 5×10^{-5} M sodium bicarbonate. All experiments were carried out at a subphase temperature of 21 ± 1 °C. Surface pressure–area (Π–A) and surface potential–area (ΔV–A) isotherm studies and LB film transfer were carried out with a KSV-5000 system mounted on antivibration table in a class 10 000 clean room. The monolayers were compressed with a barrier speed of 10 mm/min and the stability of the monolayer was inferred by holding the monolayer in the compressed state and monitoring the change in mean molecular area with time. For pure Ppy monolayers, the mean molecular area was calculated by considering the monomeric repeat unit (65 g/mol). For composite monolayers, only the amount of stearic acid was considered for calculating the mean molecular area.

BK7 glass, glass coated by an evaporated gold layer, indium–tin oxide glass, calcium fluoride, and zinc selenide plates were used as substrates that were thoroughly cleaned and dried in air prior to deposition. The transfer of composite monolayers was accomplished using the vertical dipping method at a dipping speed of typically 3 mm/min. Each deposited monolayer was dried in air for 10 min following the lifting, which was

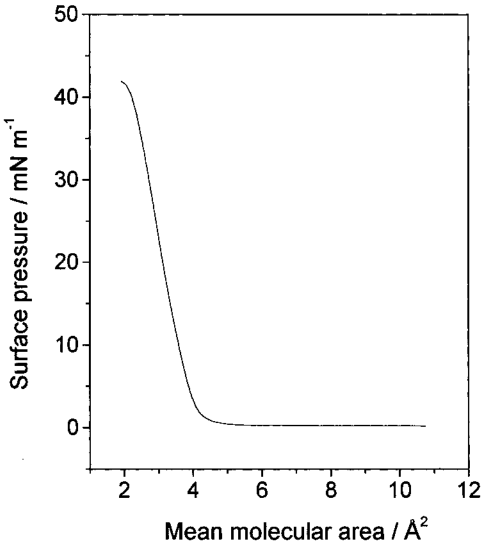

Figure 3. Surface pressure–mean molecular area isotherm of Ppy monolayer.

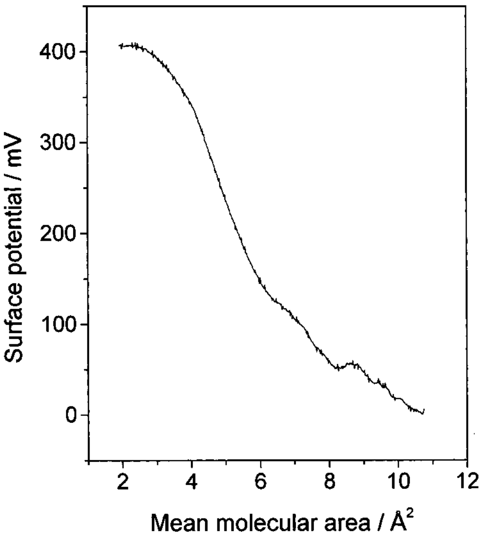

Figure 4. Surface potential–mean molecular area isotherm of Ppy monolayer.

started immediately after the dipping, without any delay inside the aqueous subphase. The Ppy monolayers were transferred at a surface pressure of 25 mN/m with a dipping speed of 3 mm/min. X-ray diffraction (XRD) measurements were carried out with a Rigaku Rotaflex-RU 200B X-ray diffractometer in the 2θ range of 3–20° using a Cu target. Lateral dc electrical conductivity measurements were carried out at room temperature with the four-probe method; the current was measured with a Keithley-167 electrometer with silver paint contacts on the top of the film. Surface potential measurements were carried out with a Trek 320B electrostatic voltmeter. Cyclic voltammetric measurements were carried out in an EG-PARK-270 potentiostat.

Results and Discussion

Monolayer characteristics of pure Ppy and mixtures of Ppy and cadmium stearate were studied. Preliminary experiments to form Langmuir monolayers of pure Ppy did not result in stable and transferable monolayers. A gradual decrease in the mean molecular area was noticed on holding the monolayer in the compressed state and brown-colored microcrystallites could be seen by naked eye on the water surface during the stability experiments. However, it has been noticed that in the subphase temperature range of 24–28 °C, a reasonably stable monolayer could be obtained. The surface pressure–mean molecular area isotherm of pure Ppy at a subphase temperature of 24 °C is shown in Figure 3. The collapse pressure is ~40 mN/m and the limiting mean molecular area is 4 Å^2, which probably indicates the formation of multilayer stacks instead of a true monolayer of Ppy. Similar observations have been made with Langmuir films of parent polyaniline.[19] The nature of the isotherm of Ppy is similar to that reported for poly-3-decylpyrrole monolayer.[10] However, the observed higher collapse pressure (~60 mN/m) and the limiting mean molecular area of about 27 Å^2 with poly-3-decylpyrrole monolayer may essentially be indicating the dominant role of alkyl chains in the monolayer packing in the case of the alkyl-derivatized polymer.

The surface potential isotherm was also recorded for the pure Ppy monolayer, as shown in Figure 4. To our knowledge this is the first time the surface potential isotherm of Ppy monolayer was investigated. The surface potential was nonzero even at very high molecular areas. After a small plateau at ~100 mV, the surface potential reached a maximum value of ~400 mV. It is known that for complex molecules such as those of preformed polymers, measured surface potentials cannot be related to group dipole moments, unlike the case of simple aliphatic compounds.[20] However, the observed rise of surface potential at larger areas is possibly related to the coming together of polymeric molecules forming large domains well before such clusters can be detected by the surface pressure measuring system. Monolayers of pure Ppy could be transferred onto solid substrates, but the resulting films were not as homogeneous as is the case of high-quality LB films. Because the transfer ratios were rather poor (0.5–0.6), the UV–vis absorption spectrum is less intense than a mixed film with the same nominal quantity of polymer, as will be discussed later.

Highly uniform LB films can nevertheless be produced if mixed monolayers are employed, in which the polymer is co-spread with a building material such as stearic acid. This method has already proven to occur for polythiophene and polyaniline.[21,22] Indeed, by adopting this mixed-film approach, we have also observed that a stable and transferable composite Ppy-cadmium stearate monolayer could be obtained. Surface pressure isotherms for the composite monolayer containing different weight percentages of cadmium stearate and soluble Ppy are shown in Figure 5. The nature of the surface pressure isotherm is of a condensed type, irrespective of the monolayer composition, and is similar to that observed with monolayers of poly-3-decyl pyrrole.[10] The similarity in these results indicate clearly that the packing properties of the mixed monolayers are mainly determined by the building material (i.e., the cadmium stearate). Indeed, as discussed later, the X-ray diffractograms for mixed LB films show the existence of cadmium stearate domains, with bilayer distances that are close to that of pure cadmium stearate LB films. The absence of any clear liquid region in the isotherm indicates that the stearic acid has been completely ionized. It should be mentioned that the isotherm of pure cadmium stearate is characterized by a steep rise in surface pressure at ~20 Å^2, with a collapse pressure of ~65 mN/m. The isotherms

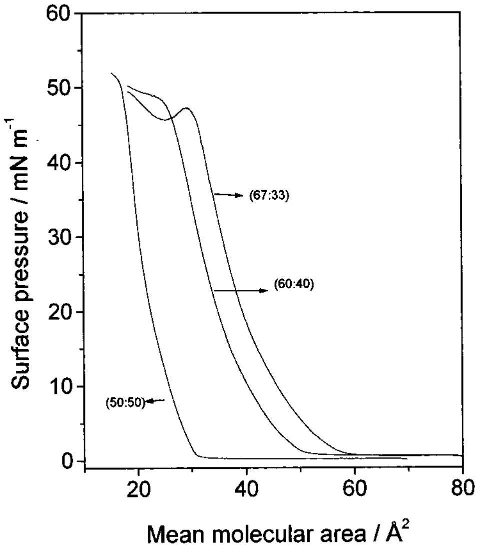

Figure 5. Surface pressure–mean molecular area isotherms of composite monolayer containing different weight percentages of Ppy and cadmium stearate. (The area is calculated in terms of the area per stearic acid molecule.)

shifted toward higher mean molecular areas with the increasing amount of Ppy in the spreading solution, which indicates that more and more polymer molecules were being accommodated in the monolayer along with cadmium stearate. The collapse pressure for these mixed monolayers is ~50 mN/m. The mean molecular area decreased at the initial stages on holding the monolayer at 30 mN/m, the surface pressure at which depositions were carried out. The initial decrease in area might be due to the squeezing out of some polymer molecules from the cadmium stearate monolayer, as it has been observed with composite monolayers of polythiophenes and polyaniline.[20,22] Indeed, the observed monolayer characteristics are very similar to those observed with composite monolayers of cadmium stearate and polyaniline.[23] The surface potential–mean molecular area isotherm of a composite monolayer containing an equimolar amount of Ppy and cadmium stearate is shown in Figure 6. The shape of the surface potential curve for the mixed monolayer is similar to that of simple compounds, with the surface potential increasing sharply at a critical area similar to that observed with pure Ppy monolayer. The maximum surface potential of ~260 mV is close to that observed with pure Ppy monolayer (the maximum surface potential observed with a pure cadmium stearate monolayer is ~120 mV), which indicates the dominant contribution from the Ppy component.

The composite monolayers could easily be transferred onto solid substrates in the form of Y-type multilayers with near unity transfer ratio. In the present study, we have deposited up to 29 layers, but the trend observed indicated that good transfer of additional layers can be achieved. The transferred films are visually quite uniform and dark brown in color. The transferred LB multilayers on BK7 glass were characterized by UV–vis spectral analysis. The UV–vis spectra of different numbers of layers of as deposited composite LB films containing cadmium stearate and Ppy are shown in Figure 7. Strong absorption is observed at ~415 and ~600 nm and there is a very weak, nearly flat absorption throughout the visible and near-IR region (absorption in the near-IR region is not shown in the figure). There are striking differences in the absorption spectra of LB films made in this study, in comparison with the spectrum obtained with the spreading solution used in the LB experiments and also with the spectrum reported for the cast films made from soluble Ppy.[17] As shown in Figure 2, although there is an enhanced absorption at ~550 nm, the absorption in the long wavelength region decreased in the case of LB films in comparison with the solution spectra. The observed difference might be due to the possible dedoping and the related conformational changes of the Ppy during the LB processing, which was essentially carried out at a subphase pH of ~6.0. The observed lower absorption for pure Ppy LB film (13 layers, curve d in Figure 2) in comparison with that of a composite LB film containing Ppy and cadmium stearate (27 layers, curve c in Figure 2) is probably due to the poor transfer of the pure Ppy monolayer. To confirm the uniform layer-by-layer transfer of Ppy, the absorbance at 415 nm was plotted against the number of layers. As shown in Figure 8, the absorbance increases linearly with the

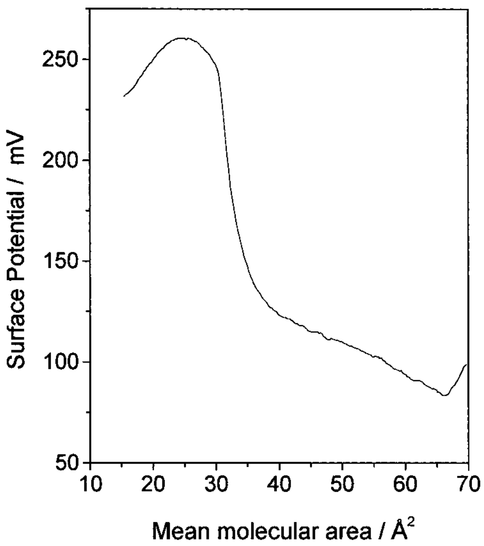

Figure 6. Surface potential–mean molecular area isotherm of composite monolayer containing Ppy and cadmium stearate (50:50 by weight; the area is calculated in terms of the area per stearic acid molecule).

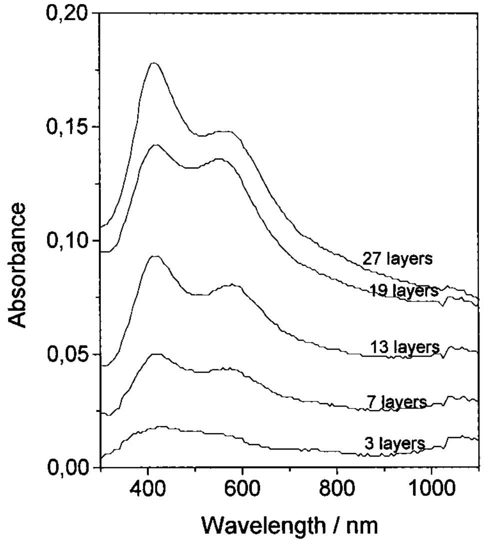

Figure 7. UV–vis absorption spectra of composite Ppy and cadmium stearate LB films containing different numbers of layers.

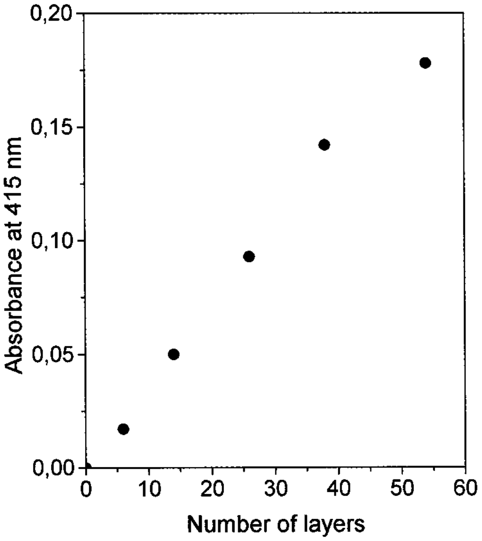

Figure 8. A plot of absorbance at 415 nm versus number of layers of composite LB films containing Ppy and cadmium stearate.

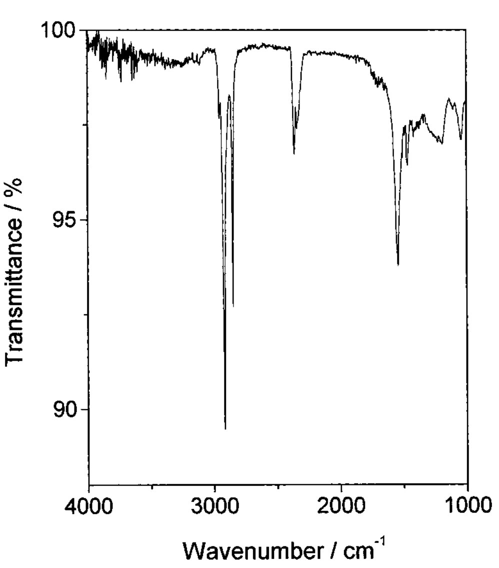

Figure 9. FTIR transmission spectrum of a 13-layer composite LB film containing Ppy and cadmium stearate.

number of deposited layers, which means that equal amounts of Ppy were transferred at each deposition step.

The multilayer LB films have also been characterized using FTIR spectroscopy. Figure 9 shows the FTIR transmission spectrum of a 13-layer as-deposited composite LB film containing Ppy on a calcium fluoride substrate. Apart from the absorption peaks corresponding to C–H stretchings (at 2916 and 2848 cm^{-1}) and bending vibrations (at 1467 and 1350 cm^{-1}), the presence of a strong characteristic peak at 1544 cm^{-1}, corresponding to C–O stretching vibrations of the carboxylate group, clearly indicates that the film mainly contained stearate salt, supporting the features observed in the isotherm curves. Also, weak but characteristic absorption peaks corresponding to ring vibrations of Ppy in the region of 1400–1000 cm^{-1} were observed, thus confirming the transfer of Ppy along with cadmium stearate. These Ppy ring absorptions are similar to those reported for the doped Ppy obtained by the oxidation of a mixture of pyrrole and alkylpyrrole at the air–water interface.[24] Consistent with the results from the UV–vis spectra, the FTIR data failed to display strong absorption in the region of 4000–2000 cm^{-1}, which is usually attributed to the presence of free charge carriers. It may be mentioned that such strong free carrier absorption in FTIR has not been found for the X-ray doped polyaniline LB films for which a clear change due to doping could be noticed in the UV–vis spectra.[25]

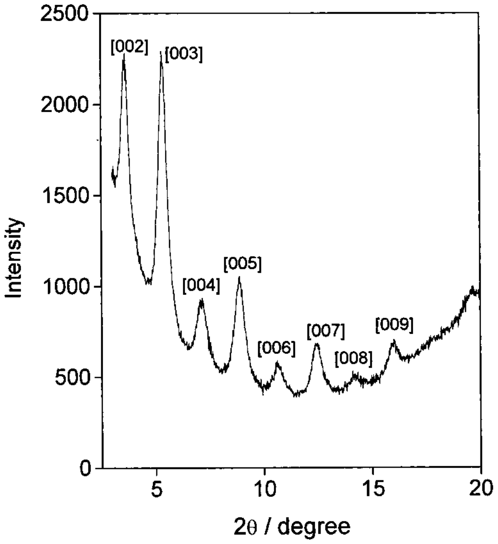

Figure 10. XRD pattern of a composite LB film (27 layers) containing Ppy and cadmium stearate.

The X-ray diffraction pattern obtained with one as-deposited composite LB film (27 layers) is shown in Figure 10. It exhibits a set of intense diffraction peaks with corresponding bilayer spacing of 49.7 ± 0.2 Å, which is very similar to that of pure cadmium stearate LB films.[1] The main difference lies in the decrease of the absolute intensities of diffraction peaks, which may be attributed to the decrease of stacking order of cadmium stearate molecules due to the incorporation of Ppy. This result probably indicates that the cadmium stearate molecules are present as separate domains in a matrix of randomly distributed polymer molecules. This feature is similar to what has been observed with composite LB films made from cadmium stearate and polyaniline[23] and polythiophene.[21]

The cyclic voltammogram (not shown) of a composite LB film containing Ppy (five layers) transferred onto ITO glass exhibited redox peaks similar to those obtained with electrochemically prepared Ppy thin films, but with comparatively broader redox peaks. Though it is known that the use of interdigited electrode assemblies provides a more accurate measurement of electrical conductivity for thin films, for the purpose of comparison with earlier results, the dc conductivity of composite Ppy LB film was measured using the standard four-probe method. The in-plane dc conductivity at room temperature was of the order of 10^{-5} S cm^{-1}. The low conductivity value may indicate that the Ppy molecules in the as-deposited composite LB film are mostly undoped, or only partially doped. Even though it is a macroscopic measurement, the surface potential of LB films is often employed to probe film uniformity as it is sensitive to very small nonhomogeneities. The surface potential for a five-layer composite LB film transferred onto a gold/glass substrate was ~180 mV. The variation in the surface potential value while scanning the whole surface of the film was only ∼10 mV, within experimental error, indicating excellent film uniformity. The surface potential is slightly lower than that of the corresponding composite monolayer at the air−water interface, possibly due to a negative contribution from the substrate−film interface.

The UV−vis, FTIR, and electrical conductivity results of multilayer composite LB films have revealed the presence of Ppy in the transferred films. The polymer apparently was less doped than in the solution employed for spreading the Langmuir monolayers. This change in the doping state might have occurred during the LB processing, as monolayers were spread on aqueous subphases of pH 6.0. Such dedoping has already been observed in the LB processing of polyaniline which had been previously doped with either camphor sulfonic acid[23] or DBSA,[26] under similar subphase conditions. Another possibility is that the filtering process in preparing the spreading solutions has eliminated some insoluble high molecular weight portions of Ppy, the remaining fraction being less doped.

Conclusions

The preparation of composite LB films of soluble Ppy has been demonstrated for the first time. The formation of stable and easily transferable composite monolayers containing cadmium stearate and Ppy has been inferred through surface pressure and surface potential isotherms and the LB film transfer process. The observed monolayer characteristics and transfer behavior are comparable to those of composite LB films of polyaniline processed with amphiphilic dopants. The characterization of transferred films revealed that Ppy in the composite LB film is less doped than in the starting spreading solution. It is also worth mentioning that although we used a similar procedure in the synthesis, the Ppy obtained in the present study displays different characteristics to those of ref 17. The main differences lie in the degree of doping that appears to be less pronounced for the Ppy produced here, as evidenced by the UV−vis spectra.

Acknowledgment. The authors are grateful to FAPESP and CNPq for financial support. They are also pleased to acknowledge Dr. L. H. C. Mattoso for providing DBSA and Mr. A. Riul Jr. for his help during the conductivity measurements. Thanks are due to Dr. Máximo S. Li (IFSC-USP) for kindly supplying CaF_2 substrates and to Asashi Company (Japan) for supplying ITO substrates.

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