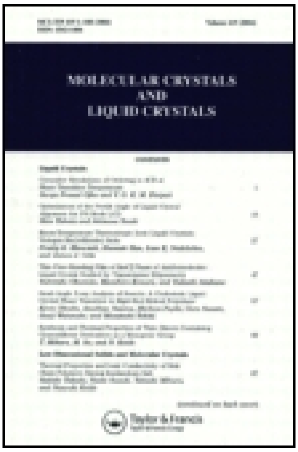

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Deposition and Characterization of Langmuir-Blodgett Films of Monomeric and Polymeric Pyrrole Derivatives

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DEPOSITION AND CHARACTERIZATION OF LANGMUIR - BLODGETT FILMS OF MONOMERIC AND POLYMERIC PYRROLE DERIVATIVES

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Abstract In this Paper we report the deposition and characterization of Langmuir-Blodgett multilayers of pyrrole derivatives in monomeric and polymeric form. The influence of monolayer preparation and deposition conditions, the quality and reproducibility of the multilayers were studied by FTIR, Brewster angle and scanning force microscopy.

INTRODUCTION

The preparation of high quality ultrathin films of polymeric conductors has great relevance for technological applications such as sensors and molecular electronics[1]. One of the most promising techniques, which allows the ordered build-up, layer by layer, of molecularly controlled architectures is the Langmuir - Blodgett (LB) deposition technique[2]. Among the most interesting molecules from this point of view are the polyheterocycles, which are electrically conductive in oxidized forms. Such molecules must be modified in order to be deposited with the LB technique. Generally alkyl tails of varying length are added at specific positions of the aromatic ring; the problem is to be sure that the molecular modification will not cause the deterioration of the electrical conductivity of the film. This requirement will generally be in conflict with the other requirement of feasibility of the LB deposition; thus an optimal equilibrium between these two conditions must be looked for.

In this Paper we present a study of LB mono- and multilayers of two pyrrole derivatives, namely 3-decylpryrrole (3DP) and 3-hexadecylpyrrole (3HDP). The films were deposited from both monomeric and polymeric monolayers. Apart from the study of the monolayer and best deposition conditions, our aim was to assess which chain length was most suitable relative to film stability, layer reproducibility and order, and conductivity characteristics of the polymeric multilayers.

EXPERIMENTAL

The amphiphilic derivatives 3DP and 3HDP were obtained by alkyl substitution on the pyrrole rings. The corresponding polymers were obtained[3] by chemical bulk polymerization under argon athmosphere, using ferric chloride ($FeCl_3$) as oxidizing agent (see fig. 1).

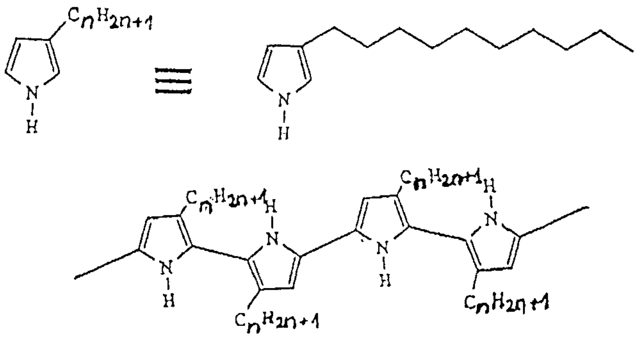


FIGURE 1. Pyrrole and poly-pyrrole derivatives (n = 10 for 3DP and P3DP, n = 16 for 3HDP and P3HDP).

Monolayers of the two monomers were obtained by spreading microquantities of solutions (1 mg/ml) in chloroform on a pure (18MΩ/cm) water subfase in the KSV5000 through. Isotherms were obtained at the temperature of 20±2°C; typical compression speed was 10-20 mm/min (≈15 cm^2/min). Deposition was performed at constant surface pressure (typically 20 mN/m) and at a vertical dipping speed of 1 to 10 mm/min.

Fourier Transform Infrared (FTIR) absorption spectra were recorded with a Bohmen Fourier transform interferometer at a resolution of 1 cm^{-1} and performing 16 scans for the samples containing more than 40 layers, 256 scans for those containing around 20 layers and 16000 scans for one monolayer and its silicon substrate.

Atomic force microscopy (AFM) images showing the planar distribution of our films on a scale of about 2.5 $\mu \times 2.5$ μ were taken in air, in equiforce mode, with scan frequencies in the range 1 - 5 Hz.

RESULTS AND DISCUSSION

Since the very beginning of our experiments, 3DP has shown to be the most critical substance. However, since we expected that 3DP molecules would yield films of better conductivity characteristics (as shorter tails introduce lower perturbations in the conductivity mechanism), we insisted in trying to deposit it. Our results, obtained with several different characterization methods, consistently showed the poor stability and homogeneity of the film. The isotherms recorded (for example, fig.2,a) were scarcely reproducible and the images obtained with AFM showed that the layers collected were very inhomogeneous. It was also verified that the thickness of monolayers didn't agree with what was expected from the molecular dimensions, showing that most likely the film folds in an glass-like structure. These problems are very likely caused by the inhomogeneous distribution of the 3DP molecules in the deposited layer. The 10 carbon atoms tails are too short to allow a sufficiently strong hydrophobic interaction between the neighbour molecules and hence no strong packing is possible. Presence of dimers and trimers in not very fresh solutions and solubility of the monomers into the subfase, due to electrostatic interactions with the water molecules, also influence negatively the monolayer.

Isobaric studies at pressures of 0, 5, 10, 15 and 25 mN/m showed that the 3DP film reaches equilibrium only after 40 minutes. Vertical transfer of such films on hydrofilic and hydrophobic glass, at the pressure of 22 mN/m, using both Y (tail to tail and head to head) and X (head to tail) configurations, was found to be not successful enough.

Six more carbon atoms along the aliphatic chain change completely the form of the isotherm, which becomes similar to already published ones[4]. Steepness and small areas per molecule in the condensed fase (about 25 Å^2) are good characteristics of the 3HDP isotherm (fig.2,b), which indicate a tightly packed and stable film. In spite of this, it was not possible to carry out an Y-type deposition; however, very good transfer ratios were obtained for the first 14 X layers deposited on a silicon wafer at a pressure of 20 mN/m, and good ones for the next 3 X layers.

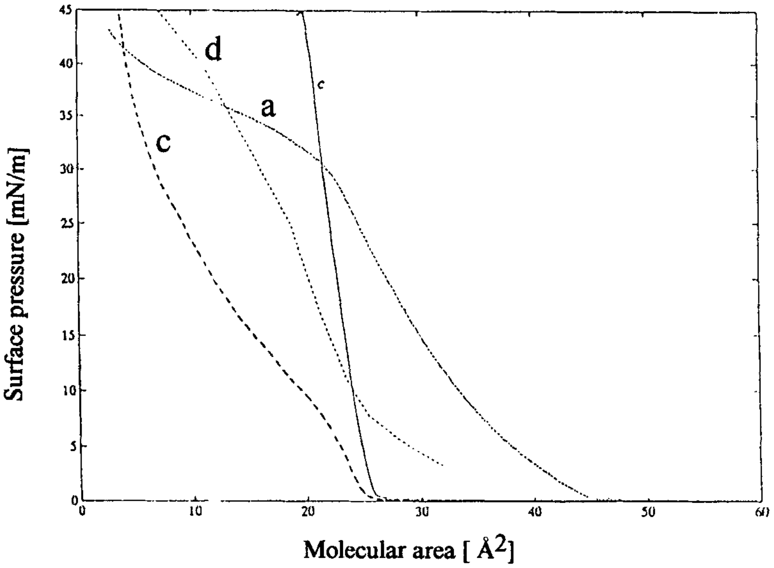
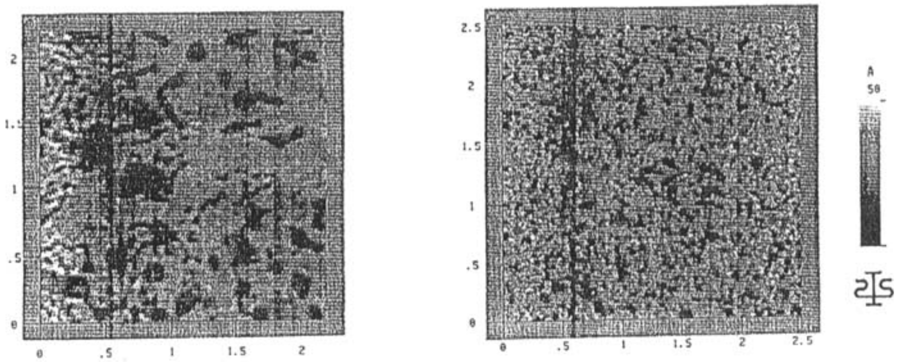


FIGURE 2. 3DP (a), 3HDP (b), P3DP (c) and P3HDP (d) isotherms on water subfase.

Polymer monolayers were also studied, using chloroform solutions of the already bulk polymerized substance. As the solubility was not complete especially for the P3HP, the solutions were filtered before their spreading on the water. It is therefore likely that only low molecular weight polymeric chains were present in the final solutions. The P3DP isotherm (fig.2,c) presents quite small areas per monomer unit, inferior to 20 Å^2. This could be due to the imperfect monolayer structure of the P3DP film, caused by some polymeric chains which do not extend completely on the water surface and hence some of the monomeric groups stay out of the subfase; another problem might be the formation of a bilayer at the air-water interface. However, images obtained with Brewster microscopy, showing an extremely homogeneous film on the scale which is accessible to the instrument, encouraged us to transfer up to 140 layers on solid substrates (glass and silicon wafers) at a pressure of 18 mN/m, with a dipping speed of 10 mm/min.

P3HDP shows, in therms of stability and homogeneity, a better behaviour than P3DP, as 3HDP does with respect to 3DP. In particular, as it can be seen in fig.2(d), the decrease in area per molecule observed for P3DP with respect to 3DP doesn't occur. This could suggest that the side carbon chains could affect the anchoring of the molecules to the subfase surface. It is likely that a greater number of carbon atoms in the chain could enhance the ordering of the molecules in a sort of lattice and this fact could make molecules all lie over the subfase.

Considering the unsatisfactory behavior of 3DP, we worked mainly on its polymer. The transfer ratios for P3DP were not satisfactory for the first 5 Y layers; indeed, AFM images obtained from 4 P3DP layers deposited vertically with a very low dipping speed (1 mm/min) onto hydrophobic glass put in evidence big holes into a quasi-homogeneous film on a coarse scale (about 40 μ × 40 μ), while from 3 Y layers transferred onto hydrophilic glass we obtained the image of a surface crossed by numerous valleys and peaks. Recent images of P3HP multilayers (fig. 3, a, dim. 2.2 μ × 2.2 μ) collected on glass show that this polymer with longer side chains appears more compact even if it presents large holes (height corresponding to one layer). On the contrary, P3DP looks like it is formed by "small" domains not joined to each other (fig. 3,b, dim. 2.5 μ × 2.5 μ).



a b

FIGURE 3. AFM images of P3HDP (a) and P3DP (b) multilayers collected on glass.

However, proceeding with the deposition, on glass and silicon wafers, until 140 P3DP layers, good transferratios were measured. Optical absorption in the UV-VIS range features the typical shift to the UV of the absorption peak of the LB films with respect to the bulk solutions of their molecules, while Brillouin spectroscopic investigations[5] showed the acustic isotropy of samples consisting of 30 and 50 P3DP layers. Such behavior implies either an orientation of the hydrophobic chains perpendicular to the solid substrate or a total disorder of these tails.

More information was obtained from FTIR absorption measurements (fig.4) carried on a stepped sample presenting coloured stripes which correspond to different number of layers (from 20 to 140), deposited on silicon. The colours are due to multiple interference of the visible light on the thin films, which have a thickness comparable to the wavelength of the light[6]. The definition and sequence of colours as a function of the number of layers are good indication of reproducibility of mass transfer and layer structure as the film is built up.

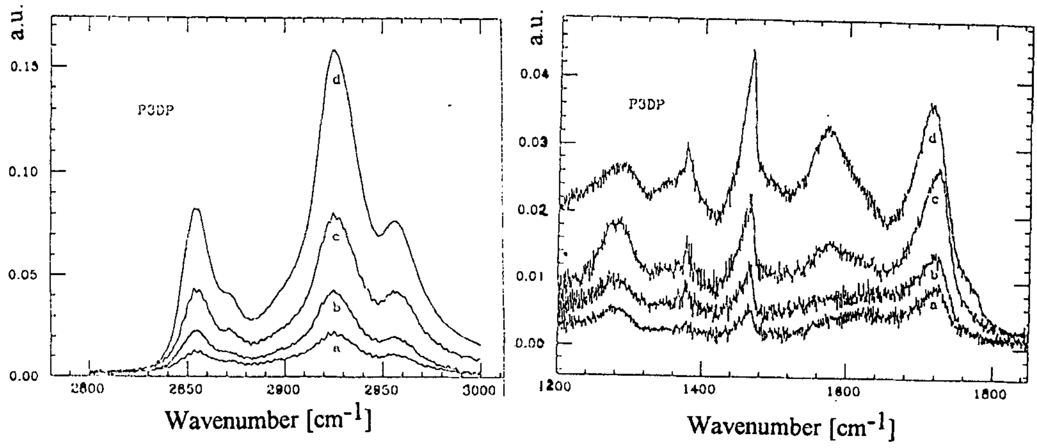


FIGURE 4. FTIR spectra of a P3DP LB sample (a: 20 layers, b: 40 layers, c: 80 layers, d: 140 layers). Left: 2800 - 3000 cm^{-1}; Right: 1200 - 1840 cm^{-1}.

The good proportionality of the optical density corresponding to the CH_2 stretching peaks *versus* the number of layers (fig.5), as well as the good transfer ratio, confirm quantitatively that equal quantities of polymer deposit during each up- and down-stroke of the solid substrate across the monolayer. Best evidence on the high order in the direction normal to the substrate, meaning a real layer by layer deposition, should have been got from X-ray diffraction measurements; unfortunately, such measurements did not show any Bragg peak[7]. Similar results revealing random organization were reported

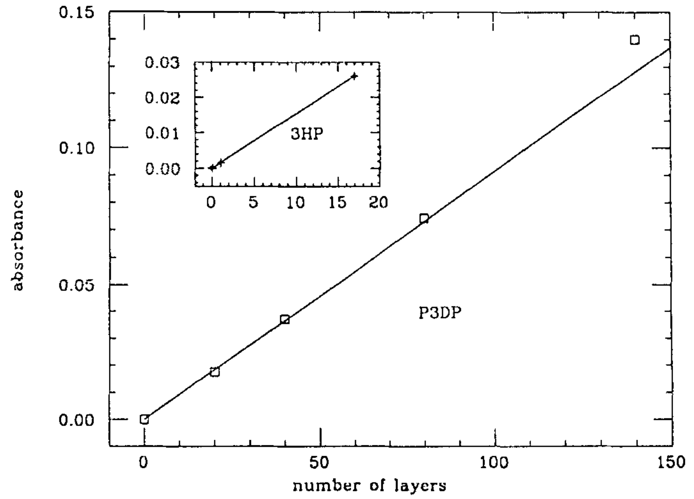


FIGURE 5. FTIR peak intensity as a function of the number of layers for P3DP and 3HDP (in the insert) multilayers.

on medium conductive and insulating LB films deposited from 3-octadecyl-pyrrole/pyrrole (from 1/5000 to 1/300 concentration ratio) monolayers with a 1% $FeCl_3$ subfase and also on highly anisotropic and conductive 3-octadecanoyl-pyrrole/pyrrole films prepeared in the same way[4].

The 100 - 1840 cm^{-1} zone presents peaks corresponding to in-plane rig deformations and to δ deformations of the methyl and methylene groups. It is similar to the spectrum reported for a 3-octadecyl-pyrrole floating monolayer[4]. One can note the presence of a strong peak at 1710 cm^{-1}, which does not appear in the solution IR spectrum, corresponding to some carbonyl groups attached to the pyrrole rings during their oxidation. Such phenomenon is not desired as it marks limits in the polymerization chain and in the conductivity of the material. The shift of this peak for the 140 layers may be a proof of the increase of the degree of disorder at such great number of multilayers. Note in particular the overall change in the structure sensitive aromatic "fingers" spectral range occurring at about 40 layers.

FTIR spectra were also recorded for 17 3HDP X layers in the same ranges. The spectrum in the range of the CH_2 vibrations (fig.6, down) has the same form as the one of 20 P3DP layers, with the only two main peaks well defined, while for the aromatic vibrations zone there is no significant signal. Comparing the ratio of the contribution to the intensity of the strongest peak from one P3DP layer and the same contribution of one 3HDP layer to the ratio of the corresponding tail lengths, we find an error of less than 10 %. This demonstrates that there is no significant difference between the number of tails (and therefore, of monomer units) in one layer of P3DP and in one of 3HDP. Similar arrangements characterize both types of films. These conclusions are confirmed by the FTIR spectrum of a one layer 3HDP sample (fig. 6, up).

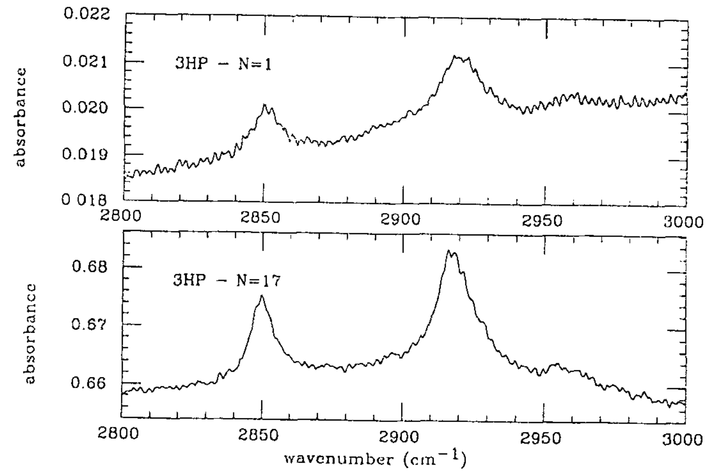


FIGURE 6. FTIR spectrum of 17 3HP layers (down) and of 1 (up) 3HDP monolayer.

Preliminary X-ray reflectometry measurements done on the 3HDP X sample revealed two superposed periodical structures, one of X-type arrangement with a latticeparameter of 60 Å^2 (indicating that the reflection planes are bilayers) and the other of Y-type with a double parameter[8]. Thus even for these molecules the multilayer structure is rather complex and this implies a strong reduction in the conductivity values[9].

CONCLUSIONS

Isotherm studies demonstrated that chains of 16 carbon atoms confer to pyrrole monomers and polymers the molecular structure mostly adapted to form monolayers at the air-water interface and then Langmuir-Blodgett films. The analys of the FTIR absorption spectra revealed a linear relationship between optical density and the number of layers up to the relatively large number of 140, thus confirming that the monolayers are reproducibly transferred onto the solid substrate; the polymer chains are oxidated, and this phenomenon decreases the conductivity of our material, whose chains structure seems to be randomly organized. However, there is not much difference between the number of monomer units in one layer of P3DP and in one of 3HP. The latter forms LB layers with a mixed X and Y structure based on successive bilayers with a thickness of 60 $Å^2$.

REFERENCES

1. See for instance John R. Ferraro, Jack M. Williams: Introduction to Synthetic Electrical Conductors, Academic Press, London (1987).
2. G. Roberts: Langmuir-Blodgett Films (1990, Plenum Press, NY); G. Gaines, Jr.: Insoluble Monolayers at Liquid-Gas Interfaces (1996, Interscience Publishers); W. Harkins: The Physical Chemistry of Surface Films (1952, Reinhold Publishing Corporation).
3. T. Ezquerra, G. Wegner: Makromol. Chem., Rapid. Commun., 10, 103, (1989).
4. R. S. Duran, H. C. Zhon: Polymer,1992, 33, Nr.19, 4019-4023; L. Samuelson, A. K. Rahman, G. P. Puglia, S. Clough, S. Tripathy, T. Inagaki, X. Q. Yang, T. A. Skotheim,Y. Okamoto: Cognition and Order in Langmuir- Blodgett Films of 3-Hexadecyl Pyrrole and Ferrocene-Derivatized Pyrrole Mixed Monolayer System (to be published); K. Hong, R. B. Rosner, M. F. Rubner: Chemistry of Materials, 1990, 2, 82-88.
5. D. Fioretto (private communication)
6. E. Wolf: Progress in Optics (1974, North-Holland Publishing Company-Amsterdam), Ch. 4, Par. 3, 174-180.
7. F. Rustichelli (private communication)
8. R. Felici et al (to be published)
9. The conductivity data will be presented in a forthcoming publication.