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**Langmuir Blodgett and STM Investigations of
Conducting Polymer Thin Films**

by

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13. ABSTRACT (Maximum 200 words) The monomer 3-hexadecyl pyrrole was spread and polymerized at air/aqueous interfaces using a Langmuir trough. During polymerization under isobaric conditions a monotonic decrease in surface area was observed; however, upon expansion and recompression of the monolayer, the surface area for the polymer was found to be larger than that of the monomer. Monomer and polymer monolayers were also transferred to solid supports and studied by STM.					
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Langmuir Blodgett and STM Investigations of Conducting Polymer Thin Films

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In this study, a 3-substituted pyrrole monomer with a 16 carbon alkyl side chain was investigated regarding its spreading and polymerization behavior on the LB trough. The transfer behavior of the polymer monolayer to solid supports is also investigated.

The chain conformations of such monolayer films may lead to interesting local anisotropic properties. Under these conditions an ideal non-intersecting 2-D random walk conformation can be formed, and built up to multiple layers by LB methods. Previous studies however, have shown that 3-alkyl pyrroles polymerize well on the Langmuir trough only when a large amount of pyrrole was dissolved in the aqueous subphase.^{1,2} The resulting thin films had very interesting properties but were not monolayers in the conventional sense. In this case, the resulting films can always have substantial numbers of defects caused by overlapping chains and thus a less well defined two-dimensional (2-D) nature.

One method of forming a true 2-D film is to polymerize a preformed highly oriented monolayer of monomer. Monolayers of some 2-alkyl anilines on a Langmuir-trough have been polymerized by this method in our lab.^{3,4}

The pyrrole monomer is easily spread at the air/water interface using a chloroform solution. A typical compression isotherm on a water subphase is shown in Figure 1.

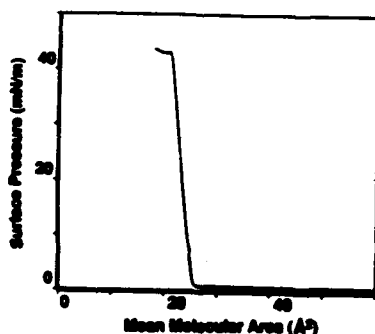


Figure 1 Isotherm of 3-hexadecyl pyrrole at an air-water interface, $T = 23^\circ\text{C}$, subphase pure water, compression barrier speed = 50 mm/min.

The 3-Hexadecyl pyrrole formed stable monolayers with a surface pressure onset point of about $25 \text{ \AA}^2$ and a monotonic increase in surface pressure with decreasing area. The monolayer collapses at about $20 \text{ \AA}^2$ with a surface pressure of about 50 mN/m. These values are comparable to those of stearic acid.⁵ Therefore, we suppose that the long alkyl chain of this monomer is well-packed in the condensed region of the isotherm with little contribution from the pyrrole ring.

Polymerization was performed on an aqueous subphase solution containing of ferric chloride (0.05 M) and sulfuric acid (0.1M) at 23°C . The surface pressure was kept constant at 15 mN/m during the reaction by displacing the barrier. Progress of the polymerization is monitored directly by measuring the surface area and instantaneous barrier displacement rate as a function of the reaction time at constant surface pressure. This is similar to a procedure used for functionalized anilines in previous publications.⁴

Figure 2 shows results from a polymerization done with the above conditions. The polymerization is seen to be complete in about 20 minutes. During the reaction, both the surface area and the barrier speed decreased as the reaction progressed.

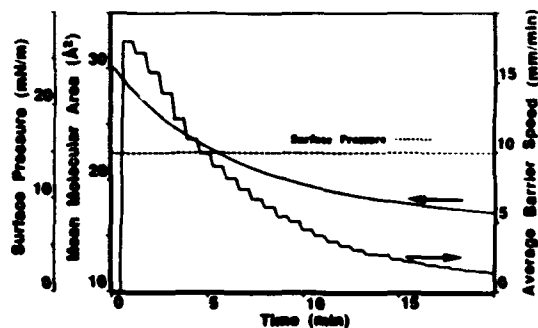


Figure 2 Polymerization of 3-hexadecyl pyrrole. Subphase 0.05 M FeCl_3 ; $T = 23^\circ\text{C}$; surface pressure of polymerization constant at $\pi = 15 \text{ mN/m}$.

After polymerization, the resulting monolayer films for both alkyl substituted compounds were stable, i.e., negligible change in surface area with time at various applied surface pressures. No reaction was observed when the pyrrole was spread on pure water and compressed. The black-greenish product produced, after extraction from the water surface, washing with pure water, and drying in a darkened dessicator, was easily soluble in THF. GPC measurements yielded a polystyrene-equivalent molecular weight average (M_w) of 5,000 to 15,000 g/mol with a considerable peak at an elution volume consistent with the pure monomer. It should be noted that if the polymer formed was left on the trough under air for several hours further oxidative degradation of the poly(3-alkyl pyrroles) occurred which decreased the polymer yield and caused the color of the products to turn brown and smaller molecular weights were measured.

The area contraction during the polymerization reaction is analogous to the volume contraction seen by dilatometry in typical bulk polymerization reactions, with the change, in part due to the replacement of a Van der Waals distances with covalent bonds. The observed decrease of about $13 \text{ \AA}^2$ per molecule is quite large, and the final surface area value of $17 \text{ \AA}^2$ per repeat unit for the polymer indicates a large conformational change of the monomer upon polymerization. Nonetheless, the mean molecular area change can be used to monitor the reaction of these substituted pyrroles in real time.

After polymerization the monolayer can be further characterized by expanding it and recompressing to observe the isotherm shown in Figure 3. On recompression, the onset point is about $28 \text{ \AA}^2$, thus larger than that of the monomer and considerably larger than that observed at the end of the reaction. In fact, the $17 \text{ \AA}^2$ surface area observed at the end of the reaction is too small to accommodate the side chains in the conformation found in conventional monolayers. The product on ferric chloride thus requires a different packing structure for the alkyl chains than just a dense ordered packing of orientationally aligned rods. Previous results on polypyrroles have indicated a helical backbone conformation is produced by polymerization in solution.⁶

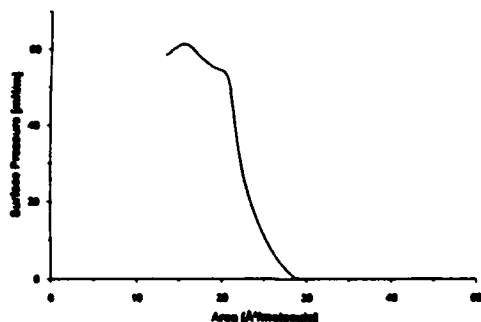


Figure 3 Compression isotherm of polymerization product of 3-hexadecyl pyrrole after expansion. Subphase 0.05 M FeCl_3 ; $T = 23^\circ\text{C}$; surface pressure of polymerization constant at $\pi = 15 \text{ mN/m}$.

We suppose that in this case, the monomer conformation changes during polymerization and the conformational nature of the polymer formed may limit the extent of polymerization on the water surface. Upon expansion the chain relaxes and more alkyl side groups find the surface again, thus the increase in observed surface area.

The monolayers were successfully transferred to solid substrates, and STM investigations of the chain conformation in the transferred layers will be discussed.

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