

Polymerization of Monolayers of 3-Substituted Pyrroles

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Derivatives of 3-substituted pyrroles were spread at the air–water interface. Stable films could be obtained for pyrroles with side chains containing more than 10 carbons. 3-Hexadecanoylpyrrole could not be polymerized as a monolayer whereas the alkyl derivatives could be polymerized successfully without having additional monomer in the subphase. The monolayers could be transferred onto hydrophobic substrates with transfer ratios close to unity. The polymers formed were soluble in chloroform and tetrahydrofuran. Molecular-weight averages obtained by gel permeation chromatography ranged from 3500 to 6000 when polymerized on ammonium peroxydisulfate and 5000 to 15000 when polymerized on ferric chloride subphase solutions. ¹H NMR indicates that the polymerization is highly regular, leading to a constitutionally ordered 2,5-poly(3-alkylpyrrole).

Introduction

Because of their air stability and high electrical conductivity, polyaniline and polypyrrole have been the focus of great attention.^{1–3} Through functionalization with appropriate side groups,⁴ or counterions,^{5,6} these otherwise poorly soluble polymers can be made soluble in common organic solvents in the neutral state or when the degree of oxidation is low. Furthermore, highly oriented thin films of these functionalized polymers can be made by the Langmuir–Blodgett (LB) technique.⁷ Preliminary work on these thin films has shown interesting anisotropic optical and electrical properties.^{8,9} Indeed, such films may prove to be useful in understanding low dimensional conductors. Some groups have successfully prepared thin films of these polymers and built up multiple layers by LB methods.^{10,11} However, 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.

A method of forming a film closer to a true 2-D nature is to polymerize a preformed highly oriented monolayer of a monomer. Under these polymerization conditions, it is hoped that a polymer conformation resulting from a

self-avoiding walk in two dimensions occurs. To date, there exists no facile experimental technique to directly confirm such a conformation. STM measurements have indicated, however,¹² that a monolayer polymerized and some rigid-rod¹³ films transferred on solid substrates do not contain overlapping chains. Monolayers of some 2-alkylanilines on a Langmuir trough have been polymerized in our lab.^{14,15} With the exception of two other reports,^{16,17} 3-alkylpyrroles have only been polymerized on the LB trough when a large amount of unsubstituted pyrrole was also present; the resulting polymer was largely unsubstituted polypyrrole from excess pyrrole monomer diffusing to the surface from the subphase.^{10,11} The resulting thin films had very interesting properties but were not monolayers in the conventional sense.

In this study, three 3-substituted pyrrole monomers with different side chain lengths and moieties were investigated regarding their spreading and polymerization behavior on the LB trough. The purpose was to find a compound that can be orientationally ordered and subsequently polymerized as a monolayer. Additionally, its polymerization product should be transferable via the LB or Langmuir–Schäfer technique onto solid substrates. The chemical structures of the investigated compounds are shown in Figure 1.

Experimental Section

The synthesis⁴ and characterization of the monomers is reported in the Supporting Information.

Monolayers and polymerization were studied using a commercially available computer-controlled film balance (KSV 5000, KSV Instruments, Finland) equipped with a floating barrier and Wilhelmy balance pressure measurement system and temperature controller. Monolayers were obtained by spreading solutions

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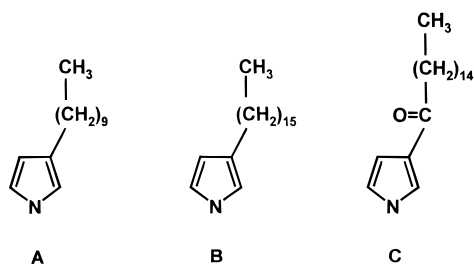


Figure 1. Chemical structures of (a) 3-decylpyrrole, (b) 3-hexadecylpyrrole, and (c) 3-hexadecanoylpyrrole.

of the monomers dissolved in chloroform (ACS Spectro Grade, Eastman) at concentrations of approximately 0.5 mg/mL. The balance was zeroed before addition.

Isotherms of surface pressure versus mean molecular area per repeat unit (Mma) were measured at 23 °C on Milli-Q water with a specific resistance of greater than 18 MΩ/cm for the monomers. For polymerization and studies of the polymer, subphase solutions were made with ACS reagent grade chemicals and Milli-Q water. Subphase oxidizing agents were ammonium peroxodisulfate (0.03 M) or a mixture of sulfuric acid (0.1 M) and ammonium peroxodisulfate (0.03 M). After polymerization, materials collected from the trough surface for further analysis were washed with water, alcohol, and again with water, then dissolved in chloroform, and after evaporation dried and stored in a desiccator under nitrogen.

The transfer of the monolayers from the Langmuir trough onto solid substrates was studied with 3-hexadecylpyrrole and its polymerization product. Different subphase solutions (oxidizing, nonoxidizing, acidic, neutral, and basic), substrate surfaces (quartz, glass, and silicon wafer—hydrophilic and hydrophobized), dipping speeds (1–50 mm/min), dipping surface pressures (0.2–40 mN/m), and polymerizing conditions (surface pressure and subphase solutions) were examined. For hydrophobization, glass or quartz plates were first soaked in Chromerge in concentrated sulfuric acid for several hours and then sonicated in ultrapure water several times. Substrates were then sonicated sequentially in each of the following solvents for about 15 min: CH₃OH, CHCl₃/CH₃OH, and CHCl₃. Substrates were then placed in a mixture of 70 mL of pure Decalin, 10 mL of CHCl₃, 20 mL of CCl₄, and 2 vol % octadecyltrichlorosilane and sonicated for 2 h. Substrates were then sonicated for 10 min in the reverse order of solvents listed above.

UV–vis spectra were recorded in chloroform solution with a Perkin-Elmer Lambda-9 spectrophotometer. IR spectra were recorded using a FTS-40A FTIR spectrometer (Bio-Rad Laboratory, MA). Gel permeation chromatography (GPC) data were collected using a Waters Associates liquid chromatograph apparatus equipped with a U6K injector and UV spectrophotometric detector from Perkin-Elmer. The sample studied was obtained by combining the results of three monolayers polymerized under the same conditions. Two Phenomenex 7.8 mm × 300 mm Phenogel 5 consecutive linear gel columns were used, a 500 Å followed by a 1000 Å type. The eluting solvent was HPLC-grade tetrahydrofuran (THF) at a flow rate of 1.0 mL/min. Retention times were calibrated using polystyrene standards. It should be noted that since the sample consisted of a mixture of several runs and no calibrations using better standards were possible, the absolute values of the molecular weights are likely to be indicative.

Results and Discussion

Monomer. All monomers could be spread at the air–water interface using a chloroform solution. Typical compression isotherms on a water subphase are shown in Figure 2.

The onset of the isotherm of 3-decylpyrrole is at a mean molecular area (Mma) per molecule of about 36 Å². The monolayer collapses at a Mma of about 21 Å²/molecule and an applied surface pressure of about 22 mN/m. The shape of the isotherm is analogous to that obtained for the same monomer at slightly different conditions and

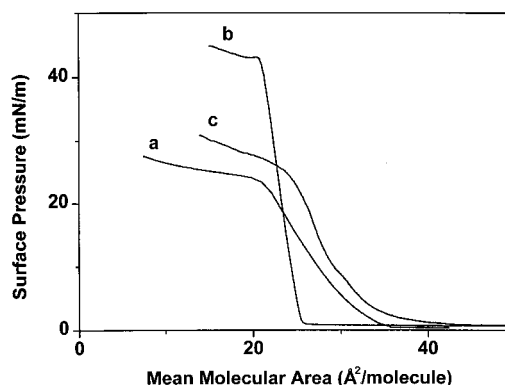


Figure 2. Isotherms of (a) 3-decylpyrrole, (b) 3-hexadecylpyrrole, and (c) 3-hexadecanoylpyrrole at an air–water interface, $T = 23$ °C, subphase pure water, compression barrier speed = 5 Å²/molecule or repeat unit/min.

that observed in similar substituted anilines.¹⁴ Hysteresis and isobaric stability measurements, however, proved that films of the 3-decyl-substituted monomer were unstable when a surface pressure was applied. The short aliphatic tail of this monomer does not render it hydrophobic enough to form a stable monolayer under compression.

3-Hexadecylpyrrole (3HDP) formed stable monolayers with a surface pressure onset of 25.6 Å². The monolayer collapse begins at about 22 Å² with a surface pressure of about 43 mN/m. This value is comparable to that obtained for the octadecylpyrrole derivative¹⁸ and a previous investigation of the hexadecyl derivative at different conditions. Synchrotron X-ray diffraction studies of the monolayers of the 3HDP monomer suggested that polar heads were packed in a distorted hexagonal packing with a tilt angle of 16.5° of the long alkyl chains (with respect to the normal of the interface).¹⁹ Therefore, it may be supposed that the long alkyl chain of this monomer is well-packed in the condensed region of the isotherm though a small contribution of the pyrrole ring has to be considered.

Figure 2 also shows the isotherm of 3-hexadecanoylpyrrole. Compared to the alkyl compound, it is shifted to higher surface areas and has a lower collapse pressure, presumably because of additional disruption of packing caused by the carbonyl group.

Polymerization. Isobaric polymerization was attempted on acidic ferric chloride and acidic and nonacidic ammonium peroxodisulfate solutions. The alkyl-substituted monomers could be polymerized, whereas no polymer could be collected for 3-hexadecanoylpyrrole. The latter may not polymerize because of the electron-withdrawing nature of the carbonyl group, or the change in surface orientation of the molecule.

The reaction at the interface is monitored directly by following the surface area change with reaction time at constant surface pressure. This is similar to a procedure used for functionalized anilines in previous publications.¹⁴

Figure 3 displays the data for the polymerization of 3-hexadecylpyrrole on a 0.03 M ammonium peroxodisulfate subphase at 23 °C where the surface pressure was kept constant at 10 mN/m. The polymerization was complete in about 20 min. During the reaction, both the surface area and the barrier speed were observed to decrease as the time of reaction increased. Independent of the reaction conditions used, similar-shaped polymer-

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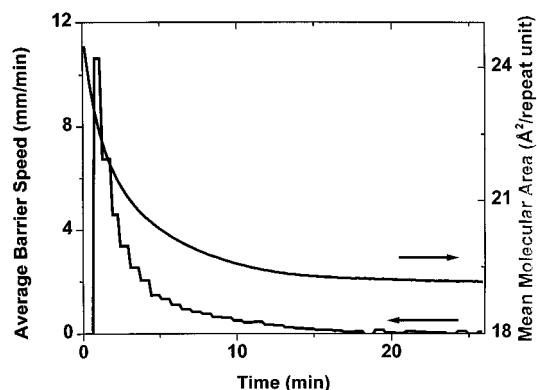


Figure 3. Polymerization of 3-hexadecylpyrrole. Subphase 0.03 M ammonium peroxodisulfate; temperature 23 °C; surface pressure of polymerization constant at $\pi = 10$ mN/m.

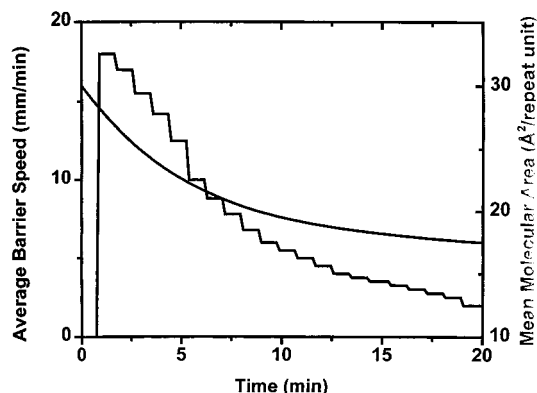


Figure 4. Polymerization of 3-hexadecylpyrrole. Subphase 0.05 M ferric chloride; temperature 23 °C; surface pressure of polymerization constant at $\pi = 15$ mN/m.

ization curves were obtained, though significantly different final surface areas were observed from the two oxidants. The above, and the shape of the curve on ferric chloride shown in Figure 4, contrast with results presented in another study,¹⁸ though both studies indicate that the pressure dependence of the reaction is complex.

The area contraction during the polymerization reaction is analogous to the volume contraction seen by dilatometry in typical polymerization reactions. After polymerization, the resulting monolayer films for both alkyl-substituted compounds were stable, that is, negligible change in molecular area with time at various applied surface pressures. There was no polymerization observed when any of the pyrrole compounds investigated here were spread on pure water and compressed.

The reduced area observed during polymerization is partly caused by the replacement of a van der Waals distance between adjacent monomers with a chemical bond due to polymerization. The area change, however, must also be indicative of a conformational change of the monomer upon polymerization.

During polymerization (with a surface pressure of 10 mN/m) on ammonium persulfate, with or without sulfuric acid, the area decreased about 5 Å²/repeat unit. The surface area 19.2 Å²/repeat unit for the polymerization product is close to that of dense-packed orientationally aligned alkyl chains. Previous results on polypyrroles have indicated that a helical backbone conformation is produced by polymerization in solution,^{20,21} which should disrupt packing of the side chains. Nonetheless, the mean mo-

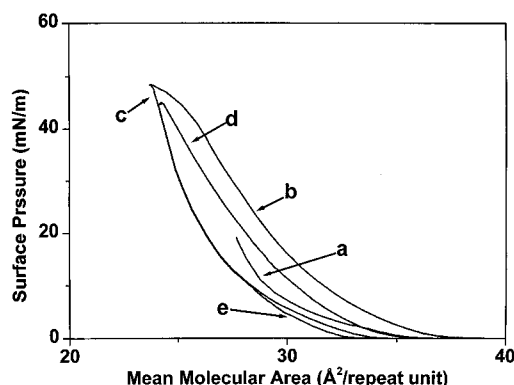


Figure 5. Data from hysteresis experiments of the monolayer polymerization product of 3-hexadecylpyrrole. Subphase 0.1 M sulfuric acid and 0.03 M ammonium persulfate. Surface pressure of polymerization was constant at 20 mN/m. (a) expansion of the monolayer directly after polymerization; (b) first compression; (c) re-expansion; (d) recompression; (e) re-expansion.

lecular area change was reproducible within 2% and can be used to monitor the reaction of these substituted pyrroles in real time.

In general, the 3-substituted pyrroles were more reactive on the LB trough than 2-substituted anilines. Unlike polyaniline, however, which shows an autoacceleration effect upon polymerization^{22,23} in this case, surface area and barrier speed decreased continuously as the polymerization progressed.

Polymer. After polymerization the monolayer can be characterized by hysteresis experiments; that is, the monolayer is repeatedly expanded and compressed. For 3-decylpyrrole the monolayer film could be expanded and recompressed with little hysteresis after polymerization. This is different from a polymerized monolayer of 3-hexadecylpyrrole, as shown in Figure 5 on a subphase containing 0.1 M sulfuric acid and 0.03 M ammonium peroxodisulfate.

When the monolayer is expanded, an increase in surface area of about 3 Å²/repeat unit is observed for the polymerization product on the ammonium persulfate subphase. The same is true for the onset point of the first recompression of the polymerized monolayer. This seems to be contradictory since during polymerization the Mma of the monomer monolayer decreased. This apparent contradiction may be explained if the polymer is assumed to be in a strained monolayer form after polymerization, but rearrange to form helices of rigid rodlike sections floating on the water surface. This type of ordering has been seen for other substituted rigid polymer backbones^{13,24,25} and is consistent with both the reported tendency of the pyrrole backbone to form a helix and the reproducible rearrangement seen on the expansion/compression cycles. The conformation adopted by the polymer after the compression cycles may not be the same as that of a monolayer of conventional low molar mass surfactants.

The resulting pyrrole polymers were characterized by several techniques. As the material is not highly oxidized, it was possible to obtain NMR spectra of the polymer. The ¹H NMR spectra of the obtained polymer is in good agreement with the proposed structure as depicted in

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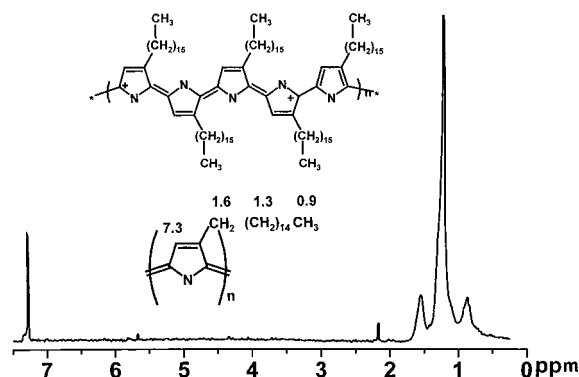


Figure 6. ^1H NMR spectrum of Langmuir monolayer polymerized 3-hexadecylpyrrole and the suggested chemical structure.

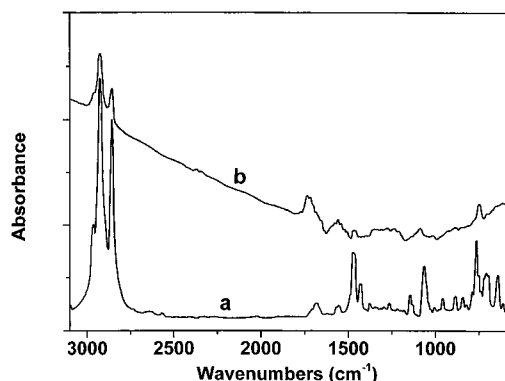


Figure 7. IR spectrum of (a) 3-hexadecylpyrrole and (b) its monolayer polymerization product in KBr.

Figure 6. It shows one peak at 7.26 ppm, which can be attributed to the proton in the 4-position of the pyrrole moiety. This indicates that the polymer formed is very highly 2,5-linked. The NMR also clearly shows signals due to the alkyl chain of the substituent. How strongly the resonance frequency of the aromatic proton is shifted depends on the degree of oxidation of the polymer backbone. There were no visible signals due to an end group.

The IR spectrum is in good agreement with that of poly-(3-alkylpyrroles) synthesized by electrochemical or conventional synthesis with ferric chloride in solution.²⁶ However, it should be noted that highly oxidized material, such as a polymer obtained by electrochemical means, shows a strong IR absorption at 4000–1600 cm^{-1} . The broad featureless band has been attributed to a free charge carrier absorption. In highly oxidized material, in fact, the intensity of this band is so strong that it completely covers the bands due to the C–H vibrations of the alkyl side chain. In the material synthesized as described here, the bands due to vibrations in the side chains are still visible. A band at 1730 wavenumbers indicates that some of the pyrrole moieties were oxidized, too. We expect this to be only a minor amount since the NMR does not indicate any additional compounds than the regular structure and the carbonyl moiety is known to have a very high extinction coefficient. These results are in agreement with corresponding studies of oxidized material in the bulk.²⁷

Figure 8 shows the UV–vis spectra of 3-hexadecylpyrrole (curve a) and its product (curve b) after the polymerization on the LB trough. Both alkyl-substituted monomers had similar UV–vis spectra, one absorption

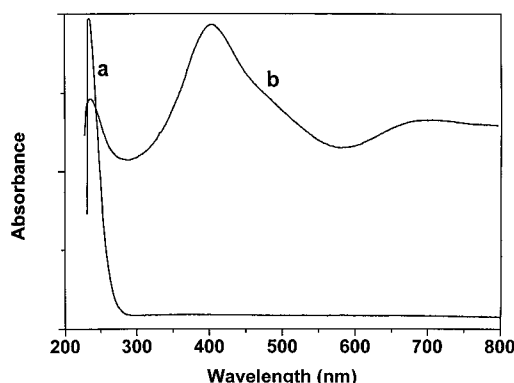


Figure 8. UV–vis spectra of (a) 3-hexadecylpyrrole and (b) its polymerization product from the LB trough in chloroform solution.

band at 235 nm. From these data it appears that the alkyl side chain length does not affect the UV–vis spectra of monomers and polymers of alkyl-substituted pyrroles. However, the UV–vis spectra of the polymers were completely different from those of the monomers and showed a broad absorbance in the range of 200–800 nm with a peak at 400 nm and a plateau at and beyond 680 nm. An additional peak at 235 nm might be attributed to unreacted monomer that is left in the product. Whereas the optical spectra of the obtained material clearly indicate that polymer is formed, they also show that the material is not highly oxidized. The spectra are in good agreement with those of poly(3-alkylpyrroles) at intermediate degrees of oxidation.²⁶ Indeed, the color of the polymer in chloroform was dark greenish, unlike the dark black color of solid polypyrrole.²⁸ If the polymer formed was left on the trough under air for several hours, further oxidative degradation of the poly(3-alkylpyrroles) occurred, which decreased the polymer yield and caused the color of the products to turn brown and smaller molecular weights were measured. This also agrees with the behavior of polypyrroles synthesized by conventional means, where also only highly oxidized material is stable under ambient conditions. With a decreasing degree of oxidation the stability strongly decreases and neutral polypyrrole derivatives degrade in air almost instantaneously.

Polymerization products under the conditions shown in Figures 3 and 4 were also analyzed by GPC. The UV detector recorded two peaks for the polymerization products: one corresponding to a monomer and the other corresponding to a low molar mass polymer with a polystyrene-equivalent molecular-weight average (M_w) of approximately 3500–6000. No third peak could be found that would correspond to the alkyl-substituted 2,5-bis-(2-pyrrolyl)pyrrolidine (BPP) which (unsubstituted BPP) was one of the main side products found in the solution polymerization of pyrrole.²⁷ The measured molecular weight depended on how long the sample was exposed to air on the trough surface or in THF solution. The M_w of the polymer from 3-decylpyrrole was also slightly higher than that for the hexadecyl moiety. However, the polystyrene calibration curve is perhaps a poor standard for the materials investigated as the polypyrrole backbone stiffens considerably at higher degrees of oxidation. The measured molecular weight only shows that a polymer is formed.

The transfer of monolayers onto solid substrates gave the following results. None of the compounds or their polymers could be transferred successfully onto hydro-

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philic substrates. Therefore, the substrates were made hydrophobic and monomer monolayers could be transferred successfully from water. Only monomer monolayers could be transferred, as on subsequent dipping the layer was transferred back to the water surface. This behavior was independent of the surface pressure and dipping speed.

For the polymer the transfer was done directly from the subphase that was used for the polymerization. If acidic subphases were used, only a monolayer could be transferred onto hydrophobized substrates. The same was observed when the subphase pH was increased with ammonia. Therefore, polymerization was done with subphase solutions containing ammonium persulfate only.

Transfer of more than monolayers of the polymerized monolayers was possible. The transfer ratio depended on the applied surface pressure while transferring and a uniform change in the trough surface area with the amount of surface transferred.

The minimum required surface pressure for the transfer was found to be above 25 mN/m. Best results were obtained with 35–40 mN/m. The barrier speed of about $1\text{--}3\text{ \AA}^2\text{ molecule}^{-1}\text{ min}^{-1}$ and the dipper speed of about $1\text{--}10\text{ mm/min}$ had to be rather slow because the polymerized layer is highly viscous.

Under these conditions subsequent dipping apparently resulted in Y-type multilayers as shown in Figure 2 in the Supporting Information. As mentioned above, the partially oxidized polymer is not highly stable in air. Therefore, multilayer structures tended to degrade in air. Within several hours after dipping, the first several micron-sized holes in the multilayer film could be observed under a standard optical polarizing microscope.

Recent STM investigations on transferred polymer monolayers of these compounds have shown no evidence of polymer chain overlap, which is an additional indication of the 2-D nature of the polymer chains formed.¹²

Conclusions

3-Alkylpyrroles could be polymerized at the air–water interface, yielding polymers that are expected to be highly ordered. The polymerization is possible without excess pyrrole in the subphase. The compounds were confirmed as polymers by NMR and GPC; however, no very high molecular weight compounds could be obtained. The reaction at the liquid–air interface could be monitored by changes in the surface area. Deposition of monolayers by the Langmuir–Blodgett technique is possible and multilayers of the polymer can be prepared. The partially oxidized polymer multilayers tended to form pinholes.

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Supporting Information Available: Synthesis of the monomers 3-decylpyrrole and 3-hexadecylpyrrole and their ^1H -NMR and ^{13}C -NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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