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Langmuir-Blodgett Manipulation of Electrically Conductive Polypyrroles

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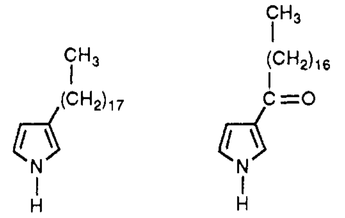
Electrically conductive polypyrroles have been synthesized at the air-water interface of a Langmuir-Blodgett film balance by spreading mixtures of pyrrole monomer and a surface-active pyrrole derivative (3-octadecylpyrrole or 3-octadecanoylpyrrole) onto a subphase containing ferric chloride. The thickness and conductivity of the resultant polymers were found to depend strongly on the mole ratio of surface-active pyrrole to pyrrole monomer used in the dispersing solvent. It is possible to create films at the air-water interface ranging in thickness from monolayer to multilayer by varying this mole ratio and the type of surface-active pyrrole added to the spreading solution. The most highly conducting films (about 10^{-1} S/cm) were produced with mole ratios of pyrrole to surface-active pyrrole approaching 5000/1. Multilayers of these films were fabricated successfully by both the horizontal and vertical lifting methods. The conductivity of multilayers formed from the 3-octadecanoylpyrrole/pyrrole system was found to be highly anisotropic, with conductivities in the plane of the film about 10^7 times greater than conductivities across the film thickness. Superlattice films comprised of electrically conductive polypyrrole rich bilayers alternating with insulating bilayers of surface-active pyrrole molecules were also fabricated.

Introduction

The field of electroactive polymers continues to witness new and significant advances related to the development of stable, processible materials with a wide range of novel optical and electrical properties.[1] As an example, consider the recent disclosures of a number of new solution- and melt-processible polyheterocycles that are electrically conductive in their oxidized forms.[2,3] The driving force for these new developments is a clearly recognized need for materials that can be manipulated into technologically useful forms such as fibers and thin films with well-defined and controllable molecular organizations. Toward this latter goal, we have been examining the use of the Langmuir-Blodgett (LB) technique as a means to process conjugated polymers into multilayer thin-film structures. This technique provides, for the first time, an opportunity to control the thickness and supermolecular organization of electroactive polymers at the molecular level. To date, we have established two different techniques suitable for the LB manipulation of the poly(3-alkylthiophenes)[4] and polypyrrole.[5] It has also recently been demonstrated[6-8] that the LB technique can be utilized to process a variety of different electrically conductive polymeric systems into multilayer thin films.

Chart I. Structures of Surface-Active Pyrrole Monomers



3ODP (1) 3ODOP (2)

In a previous publication,[5] we demonstrated that electrically conductive polypyrrole films could be formed at the air-water interface of an LB trough by simply dispersing a solution containing a surface-active pyrrole monomer and a large excess of pyrrole onto a subphase containing ferric chloride ($FeCl_3$). The ferric chloride acts to both polymerize the mixture at the air-water interface and simultaneously oxidize the resultant polymer, thereby rendering it electrically conductive. Pyrrole monomer is needed to facilitate polymerization at the air-water interface as neither the surface-active pyrrole monomer nor pure pyrrole will polymerize independently under the conditions used to prepare the films. A large molar excess of pyrrole monomer is used due to the high degree of water solubility exhibited by this material. We have recently found that the chemistry initiated at the air-water interface and the properties of the resultant polymer are strongly influenced by the type of surface-active pyrrole monomer utilized in the spreading solution. In this paper, we compare the structure and properties of polypyrrole thin films prepared from spreading solutions containing either 3-octadecylpyrrole (3ODP, 1) or 3-octadecanoylpyrrole (3ODOP, 2) as the surface-active component. The structures of these monomers are shown in Chart I. The LB manipulation of these materials into multilayer thin films and organic superlattices is also discussed.

Experimental Section

The synthesis of the surface-active pyrrole monomers used in this study and the basic polymerization procedure have been described in detail elsewhere.[5] Polymerization was carried out on the water surface of a Lauda film balance at 20 °C by spreading a solution of pyrrole and substituted pyrrole onto a subphase containing 1 wt % ferric chloride. After polymerization, the

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(1) See for example: *Proceedings of Synthetic Metals, International Conference on Science and Technology of Synthetic Metals* **1982**, 28.

(2) (a) Elsenbaumer, R. L.; Jen, K. Y.; Oboodi, R. *Synth. Met.* **1986**, *15*, 169. (b) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212.

(3) (a) Sugimoto, R.; Takeda, S.; Gu, H. B.; Yoshino, K. *Chem. Express.* **1986**, *1*, 635. (b) Sato, M.; Tanaka, S.; Kaeriyama, K. *J. Chem. Soc., Chem. Commun.* **1986**, 87.

(4) (a) Watanabe, I.; Hong, K.; Rubner, M. F. *J. Chem. Soc., Chem. Commun.* **1989**, 123. (b) Watanabe, I.; Hong, K.; Rubner, M. F.; Loh, I. H. *Synth. Met.* **1989**, *28*, C473. (c) Watanabe, I.; Hong, K.; Rubner, M. F. *Thin Solid Films*, in press.

(5) (a) Hong, K.; Rubner, M. F. *Thin Solid Films* **1988**, *160*, 187. (b) Hong, K.; Rubner, M. F. *Thin Solid Films*, in press.

(6) Shimidzu, T.; Iyoda, T.; Ando, M.; Ohtani, A.; Kaneko, T.; Honda, K. *Thin Solid Films* **1988**, *160*, 67.

(7) Nishikata, Y.; Kakimoto, M.; Imai, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 1040.

(8) Logsdon, P. B.; Jiripfleger; Prasad, P. N. *Synth. Met.* **1988**, *26*, 369.

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oxidative ferric chloride subphase was removed and replaced with fresh, purified water. This was accomplished by carefully adding new subphase at one end of the trough and removing the original subphase at the other. Specifically, a 1-L glass reservoir was connected to the trough (via a Teflon tube) close to the floating barrier. As the new subphase solution was added to the trough from this reservoir, an equal volume of subphase was simultaneously removed through a system of glass tubes, one extending to the bottom of the dipping well and another placed on the other end of the trough. With this procedure, the monolayer films were washed with 2 L of a 5% HCl solution followed by 3 L of pure water. Although most of the oxidizing agent was removed, the subphase remained acidic (typically of pH 2) due to the presence of residual acid. Care was taken to ensure that the monolayer film was not disturbed by the washing procedure.

Monolayers were transferred onto solid substrates as Y-type LB films at 25 mN/m and 20 °C. A dipping speed of 5 mm/min was used to transfer the films. Drying times of at least 2 h were used between the first and second dips. This time was reduced to 1 h for all subsequent dips. In some cases, films were transferred via the horizontal dipping technique using procedures described in the literature.[9] Film thicknesses were estimated with a surface profilometer (Dektak) on multilayer thin films with thicknesses greater than 2000 Å, which allowed determination of the average thickness per monolayer to an accuracy of about ±5 Å. Calculations of the limiting area per molecule and the pressure–area isotherms presented in this paper are based solely on the amount of surface-active pyrrole monomer dispersed on the water surface.

In-plane conductivities were measured at room temperature by using the standard four-probe technique[10] utilizing the van der Pauw configuration. Transverse conductivities were determined from measurements made on films deposited onto platinum-coated glass slides. Two methods were employed in making the electrical contacts to the top of the film, one involving an array of aluminum electrodes, the second a mercury drop. In the former case, a series of aluminum electrodes 0.02 and 0.04 cm^2 in area and 500 Å thick were evaporated onto the surface of the film. Contact was then made to the top aluminum electrodes with a fine gold wire. The second type of contact was produced by simply resting a small drop of mercury on the film surface and dipping a gold wire into that drop.

Results and Discussion

Monolayer and Multilayer Formation of the Surface-Active Pyrroles. The key to creating electrically conductive polypyrroles that can be readily manipulated into multilayer structures by using the LB technique lies with the proper choice of surface-active pyrrole. Both of the surface-active pyrrole monomers used in this study form very stable condensed monolayers at the air–water interface which can be readily transferred by using a conventional vertical LB transfer technique into highly ordered Y-type multilayer thin films. X-ray diffraction analysis of the 3ODP multilayer films indicates that the molecular layers stack with a bilayer repeating distance of about 55 Å (27.5 Å/layer). Near-edge X-ray absorption fine structure spectroscopy (NEXAFS)[11] and reflection/absorption FTIR measurements[12] have also revealed that the molecules are well ordered within the multilayer films with their fully extended hydrocarbon tails aligned nearly normal to the plane of the substrate (based on CPK models, a fully extended 3ODP or 3ODOP molecule is about 28.4 Å from end to end). In the case of the 3ODOP molecules, the hydrocarbon tails are also well aligned in the multilayer films, whereas the pyrrole head groups are actually oriented almost parallel to the substrate throughout the entire multilayer film.[12] This unusual parallel arrangement of the head groups is a direct consequence of the strong hydrogen bonding possible between adjacent molecules via the carbonyl group attached to the pyrrole ring and the N–H group of the pyrrole ring. The ability of these molecules to form stable condensed monolayers and highly ordered multilayers makes them ideally suited for the preparation of electrically conductive polypyrrole LB films. The process of converting the monomer assemblies into their polymeric counterparts, however, ultimately determines whether or not the monomer is suitable for this task.

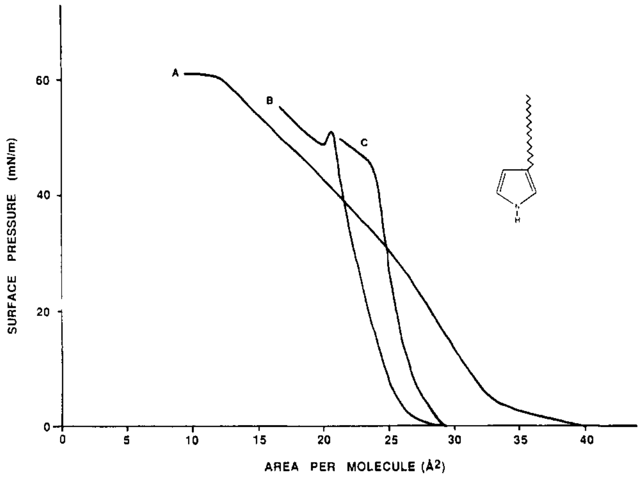

Figure 1. Pressure–area isotherms of a 5000/1 mole ratio of pyrrole/3ODP on a 1% ferric chloride subphase (A), 3-octadecylpyrrole on a pure water subphase (B), and a 300/1 mole ratio of pyrrole/3ODP on a 1% ferric chloride subphase (C). Inset shows the chemical structure of 3-octadecylpyrrole.

Direct polymerization of the surface-active pyrrole monolayers at the air–water interface via the introduction of an oxidizing agent into the water subphase is not possible due to chemical side reactions (to be discussed) and steric restrictions. Thus, it is necessary to introduce a large molar excess of pyrrole monomer into the spreading solution to facilitate polymerization at the air–water interface. The effect of the added pyrrole is highly dependent on the type of surface-active monomer codispersed at the interface. A detailed description of the differences between the two surface-active monomers used in this study is presented below.

Monolayer and Multilayer Formation of the Pyrrole/3ODP System. Figure 1 displays the pressure–area isotherms obtained from polymer films created by spreading mixtures of 3ODP and pyrrole onto a subphase containing 1% FeCl$_3$. It should be noted that previous studies[5] have revealed that the 3ODP monomer forms an insoluble polymeric film with the added pyrrole only when the mole ratio of pyrrole to 3ODP exceeds about 300/1. Also included in this figure for comparison is the pressure–area isotherm of pure 3ODP spread onto a pure water subphase. As can be seen, the isotherm of the monomer on a water subphase indicates that the 3ODP molecules pack in a condensed monolayer organization with a limiting area per molecule (obtained by extrapolating the steepest part of the isotherm to zero surface pressure) of about 24 Å^2/molecule. When pyrrole is added to the carrier solution in a molar ratio of 300/1 (pyrrole/3ODP) and the solution

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[9] (a) Langmuir, I.; Schaefer, V. J. *J. Am. Chem. Soc.* **1938**, *60*, 1351. (b) Fukuda, K.; Nakahara, H.; Kato, T. *J. Colloid Interface Sci.* **1976**, *54*, 430. (c) Nakahara, H.; Fukuda, K. *J. Colloid Interface Sci.* **1979**, *69*, 24.

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[11] (a) Skotheim, T. A.; Yang, X. Q.; Chen, J.; Hale, P. D.; Inigaki, T.; Samuelsen, L.; Tripathy, S.; Hong, K.; Rubner, M. F.; den Boer, M. L.; Okamoto, Y. *Synth. Met.* **1989**, *28*, C229. (b) Yang, X. Q.; Chen, J.; Hale, P. D.; Inigaki, T.; Skotheim, T. A.; Okamoto, Y.; Samuelsen, L.; Tripathy, S.; Hong, K.; Rubner, M. F.; den Boer, M. L. *Synth. Met.* **1989**, *28*, C251.

[12] Cheung, J.; Hong, K.; Rosner, R. B.; Rubner, M. F., results to be published.

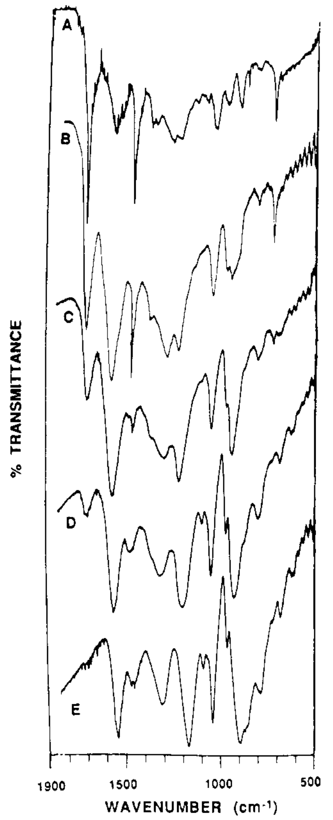

Figure 2. FTIR spectra of films prepared at the air–water interface from pure 3-octadecylpyrrole (A), from pyrrole/3ODP mole ratios of 300/1 (B), 1000/1 (C), and 5000/1 (D), all spread onto subphases containing 1% ferric chloride, and polypyrrole prepared chemically (E).

is dispersed onto a subphase containing 1% $FeCl_3$, the resultant isotherm remains about the same although it has become slightly steeper and the limiting area per molecule has expanded to about 27 Å^2/molecule (a similar isotherm is obtained when a solution containing only 3ODP is spread onto the $FeCl_3$ subphase). The isotherm generated from the polymer film created from a solution containing a 5000/1 mole ratio, on the other hand, has become poorly defined and extends over a very broad area per molecule range. These results indicate that the packing of the 3ODP molecules in their condensed phase at the water surface is only marginally influenced when polymer is formed from a 300/1 mole ratio but quite dramatically changed when polymer is formed from a 5000/1 mole ratio. The isotherm generated from the latter surface film is characteristic of a rigid, poorly organized polymer film.

To probe the structure of the material formed at the air-water interface, films created from pyrrole/3ODP mixtures with various mole ratios were prepared on a 1% $FeCl_3$ subphase and subsequently skimmed onto ZnSe plates for FTIR analysis. Figure 2 displays a series of FTIR spectra in the fingerprint region from 1900 to 500 cm^{-1} for five different systems. The top curve, labeled A, is for the 3ODP system without any added pyrrole. The three curves in the center, designated B–D, are for mixtures of pyrrole/3ODOP with mole ratios of 300/1, 1000/1, and 5000/1 respectively. Curve E is from a polypyrrole sample that was chemically prepared by applying excess pyrrole monomer onto a 10 wt % aqueous $FeCl_3$ solution by using a method similar to that described by Bocchi.[13] Since this latter technique is known to produce a highly conducting form of polypyrrole, this material serves as a excellent reference for comparison with the materials synthesized on the LB trough.

In the case of the film created from only 3ODP (curve A), the spectrum exhibits a strong absorption band at around 1470 cm^{-1} attributable to the characteristic bending vibration of the methylene groups present in the hydrocarbon tails of the 3ODP molecules, as well as a number of weaker pyrrole ring vibrations and deformations between 600 and 1600 cm^{-1}. The intensities and positions of these latter bands relative to those of the starting monomer (spectrum not shown) indicate that a small amount of polymerization (or oligomer formation) has occurred between the 3ODP molecules. Specifically, many of the heterocyclic ring vibrations have undergone significant increases in intensity presumably due to the creation of doped polymer chains and the resulting enhancement of oscillator strengths of the backbone skeletal vibrations. This latter doping-induced effect is well documented in the literature for a number of conjugated polymers.[14] Also note, however, that there is a very strong absorption band at around 1710 cm^{-1}, which can be assigned to newly created carbonyl groups on some of the pyrrole rings. Thus, in addition to polymerization, many of the pyrrole rings are also chemically modified by the oxidizing solution. The creation of carbonyl groups on pyrrole rings during chemical and electrochemical polymerization has been observed many times with various pyrrole monomers and is believed to be the result of oxidation of the pyrrole ring leading to the formation of chain-terminating pyrrolidinone type structures.[15] The observance of such a strong carbonyl absorption indicates that this latter chemistry is dominating the reaction that occurs at the air–water interface between the 3ODP molecules. This chain-terminating side reaction would therefore be expected to severely limit the degree of polymerization of the polymer and prevent the material from achieving a high electrical conductivity.

The spectra of the materials formed at the air–water interface change quite dramatically when pyrrole is added to the spreading solution. The addition of pyrrole promotes the polymerization reaction as indicated by the increase in intensity of those peaks associated with an oxidized polypyrrole backbone with increasing mole ratio of pyrrole/3ODP. In fact, the film synthesized with a mole ratio of 5000/1 exhibits an infrared spectrum very similar to that of chemically prepared polypyrrole (curve E). As the amount of pyrrole in the mixture is increased, the polymer backbone related absorption bands increase dramatically and the bands associated with the carbonyl and methylene groups appear to diminish as they are overcome by the backbone vibrations. The emergence of a spectrum dominated by vibrational bands common only to pure polypyrrole indicates that a large amount of polypyrrole homopolymer is being formed at the air–water interface. It should be emphasized that pure pyrrole will not polymerize at the air–water interface without the presence of a surface-active pyrrole monomer. The insolubility of all films made with a feed mole ratio of at least 300/1, however, also suggests that some of 3ODP molecules are reacting with pyrrole to form a copolymer. Evidence for copolymerization is also provided by a closer examination of the FTIR spectra. For example, it can clearly

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(13) Bocchi, V.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1986**, 148.

(14) See, for example: Skotheim, T. A., Ed.; *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986.

(15) (a) Salmon, M.; Kanazawa, K. K.; Diaz, A. F.; Krounbi, M. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 187. (b) Cheung, K. M.; Bloor, D.; Stevens, G. C. *Polymer* **1988**, *29*, 1709.

be seen that the positions of the absorption bands attributed to the oxidized polymer backbone (note, for example, bands near 1550, 1300, 1200, and 900 cm^{-1}) shift continuously to both higher and lower energies with increasing mole ratio of pyrrole/3ODP, eventually approaching the energies of the corresponding bands of the pure polypyrrole sample. This latter observation indicates that the structure and/or conjugation length of the resultant polymer is influenced by the molar ratio of the starting monomers. This, in turn, suggests that either the 3ODP pyrrole monomer is copolymerizing with pyrrole or that it is acting as a chain initiator or terminator, thereby becoming part of the polypyrrole chain.

The conclusion that 3ODP is incorporated within the polypyrrole chains is further supported by the results of chloroform extraction studies, where it was found that the FTIR spectra of all films (including the 300/1 film) before and after extraction were exactly the same. Specifically, the infrared absorption bands originating from the methylene groups of the hydrocarbon tail of the 3ODP molecules were found to remained unchanged, indicating that the 3ODP molecules are chemically bound to the polymer and cannot be extracted with organic solvents. It should also be pointed out that LB films made from pure 3ODP dispersed onto a $FeCl_3$ subphase are completely soluble in chloroform. Thus, pyrrole and 3ODP both react at the air–water interface to form a polymeric film that at high pyrrole contents is comprised mostly of polypyrrole-rich material. As will become evident, the fact that a reaction is possible between pyrrole and 3ODP at the air–water interface has negative consequences on the level of electrical conductivity achievable with this system.

The surface films formed at the air–water interface with the 3ODP/pyrrole system are extremely rigid and can be transferred into multilayer thin films only by using the horizontal lifting method. In addition, the electrical conductivities of these multilayer thin films only reach respectable levels, between 10^{-3} and 10^{-2} S/cm, when the pyrrole/3ODP ratio is close to 5000/1. Multilayer films fabricated from polymer synthesized with lower mole ratios are essentially insulating. It has also been found that the thickness contributed per monolayer to the transferred films varies from that expected for a monolayer of 3ODP (about 30 Å/layer) to much higher values (up to about 200 Å/layer) as the ratio of pyrrole to 3ODP increases from 300/1 to 5000/1. Clearly the added thickness per layer at the higher mole ratios is due to the formation of a large amount of polypyrrole homopolymer. The electrically conductive surface films created from the 5000/1 mole ratio feed solution are therefore not true monolayers and are best described as uniform thick films (typically 150 Å thick) of polypyrrole floating on the water surface. X-ray diffraction analysis and NEXAFS spectroscopy[11] have also revealed that the multilayers fabricated from the surface films are randomly ordered and exhibit no well-defined layered structure.

Figure 3 displays visible–near-infrared absorption spectra of LB multilayer films (containing 10 layers) fabricated from surface films formed at the air–water interface from spreading solutions containing a 5000/1 (curve A) or a 300/1 (curve C) mole ratio of pyrrole to 3ODP. Also included in this figure for comparison is the spectrum of an electrically conductive (about 1 S/cm) thin film of polypyrrole homopolymer (curve B) chemically synthesized by using ferric chloride. As can be seen, the copolymer/homopolymer mixture formed with a mole ratio of 5000/1 and the chemically prepared polypyrrole both exhibit broad absorbances that extend deep into the near-infrared region of the spectrum. These broad bands are characteristic of electrically conductive polypyrroles and are generally attributed to the existence of bipolarons.[14] The position of the peak maximum at higher energies for the LB-prepared polymer relative to the chemically prepared polypyrrole is consistent with the lower conductivity observed for the former material. The copolymer formed with a 300/1 mole ratio of pyrrole/3ODP, on the other hand, exhibits a much higher energy absorption band that only tails into the near-infrared region, thus confirming the more insulating nature of this material. Conductivity and optical measurements therefore indicate that electrically conductive polymer is created only at the air–water interface when a sufficient amount of pyrrole is present to overcome the deleterious effects resulting from reaction with 3ODP and its oxidized byproducts.

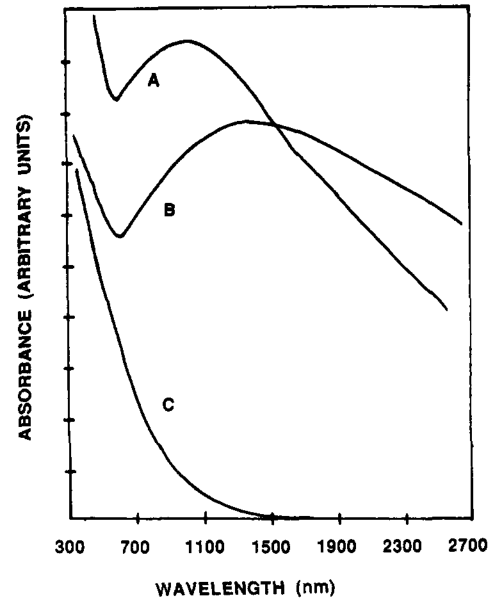

Figure 3. Optical absorption spectra of 5000/1 pyrrole/3ODP spread onto a 1% $FeCl_3$ subphase (A), polypyrrole prepared chemically (B), and a 300/1 pyrrole/3ODP mixture also spread onto the oxidizing subphase (C).

Monolayer and Multilayer Formation of the Pyrrole/3ODOP System. Although the above polymerization scheme can be utilized to form uniform thickness, electrically conductive surface films of polypyrroles at the air–water interface, the high degree of rigidity of the resultant films makes it very difficult to fabricate multilayers from these copolymers. To circumvent this problem, it was decided to utilize 3ODOP as the surface-active monomer in conjunction with excess pyrrole to form electrically conductive monolayers. As mentioned earlier, 3ODOP monomer also forms a stable condensed monolayer on the water surface of a LB trough, which in turn can be readily transferred into well-ordered Y-type multilayer thin films. In contrast to 3ODP however, this monomer does not react with ferric chloride, since the electron-withdrawing carbonyl group attached directly to the pyrrole ring deactivates the monomer to chemical oxidation. Thus, by utilizing this particular surface-active monomer, it is possible to limit the polymerization reaction solely to the homopolymerization of pyrrole monomer. In this case, the surface active pyrrole simply provides an environment at the air–water interface suitable for the polymerization of pyrrole and enhances the spreading of the resultant electrically conductive polymer into uniform monolayer films.

Figure 4 displays the pressure–area isotherms obtained from monolayer films created by spreading solutions containing a 5000/1 mole ratio of pyrrole/3ODOP onto a

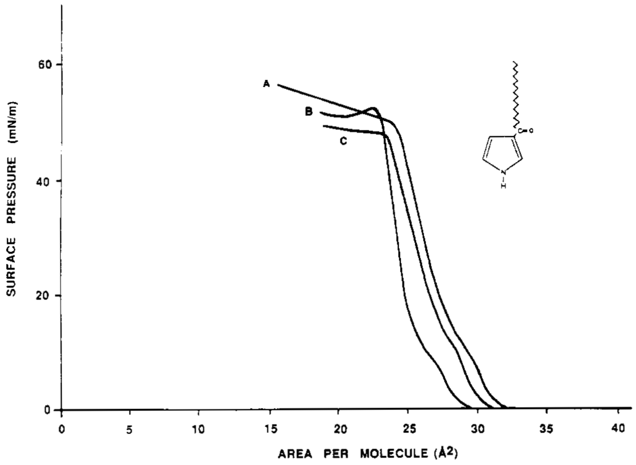

Figure 4. Pressure–area isotherms of a 5000/1 mole ratio of pyrrole/3ODOP diluted with an equal volume of chloroform and spread on a 1% ferric chloride subphase (A), 3-octadecanoyl pyrrole on a pure water subphase (B), and a 5000/1 mole ratio of pyrrole/3ODOP spread without chloroform onto the oxidizing subphase (C). Inset shows the chemical structure of 3-octadecanoyl pyrrole.

subphase containing 1% $FeCl_3$. In one case, pyrrole monomer was used directly as the spreading solvent, while in the other a mixture of 5000/1 pyrrole/3ODOP was diluted with an equal amount of chloroform to give an effective 3ODOP concentration of 0.5 mg/mL. Also included in this figure for comparison is the pressure–area isotherm of pure 3ODOP spread onto a water subphase. As was the case for 3ODP, it can be seen that pure 3ODOP forms tightly packed condensed monolayers on a pure water subphase with a limiting area per molecule of about 26 Å²/molecule. Also note the presence of a low-pressure transition around 8 mN/m that appears in all of the isotherms presented in Figure 4. This low-pressure transition along with the relatively large limiting area per molecule (compared to, for example, stearic acid) is most likely a consequence of the strong hydrogen-bonding interactions possible between molecules of 3ODOP. Optimization of such interactions could promote pressure-induced head-group reorganizations at the air–water interface and would be expected to modify the close packing of the molecules in the condensed state. It is possible that at low pressures, the head groups lie nearly flat on the water surface but are forced to align vertically at elevated surface pressures to accommodate the packing of the hydrocarbon tail groups.

The pressure–area isotherms of the monolayers formed on the oxidizing $FeCl_3$ subphase look remarkably similar to the isotherm of the pure 3ODOP (in fact monolayers formed from solutions with less than a 5000/1 mole ratio are essentially identical). The limiting area per molecule has expanded to a region between 28 and 29 Å²/molecule (depending on the spreading solvent), but the collapse pressure and general features of the isotherm are very similar to the starting monomer. This was clearly not the case for surface films formed from the 5000/1 pyrrole/3ODP system, which, as mentioned earlier, does not form true monolayers. The effect of diluting the reactants with chloroform rather than using pure pyrrole as the carrier solvent is only to slightly modify the limiting area per molecule. Thus, these data indicate that the 3ODOP molecules are not reacting with the pyrrole monomer during spreading and are therefore free to assume their normal molecular organization on the water surface. The expansion of the limiting area per molecule to larger values and the slight modification of the isotherm, however, both suggest that some chemistry has taken place. To determine the origin of these changes, we again turned to FTIR spectroscopy.

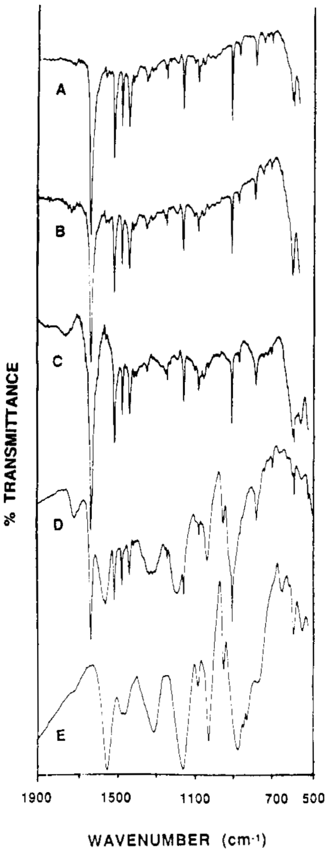

Figure 5. FTIR spectra of films prepared at the air–water interface from 3-octadecanoyl pyrrole (A), from pyrrole/3ODOP mole ratios of 300/1 (B), 1000/1 (C), and 5000/1 (D), all spread onto subphases containing 1% ferric chloride, and polypyrrole prepared in the bulk (E).

Figure 5 displays FTIR spectra obtained on films formed at the air–water interface (1% $FeCl_3$ subphase) from solutions containing various mole ratios of pyrrole and 3ODOP. The spectrum for 3ODOP without pyrrole monomer added to the spreading solution is displayed on the top, followed by spectra for pyrrole/3ODOP molar ratios of 300/1, 1000/1, and 5000/1. Also included is the spectrum for chemically prepared polypyrrole. In contrast to the case of 3ODP, the spectrum of the 3ODOP monomer does not undergo any significant changes until solutions containing a mole ratio of 5000/1 are spread onto the subphase. Even in this latter case, the spectrum appears to be a simple superposition of a spectrum of polypyrrole and unreacted 3ODOP. To verify that the film formed from the 5000/1 mole ratio solution was indeed made up of two independent components (unreacted 3ODOP and polypyrrole), additional solvent extraction studies were carried out.

The complete FTIR spectrum of the film prepared from a 5000/1 pyrrole/3ODOP spreading solution is shown in Figure 6. Also displayed in this figure is the spectrum obtained after extracting the film with warm chloroform for 10 min and a spectrum of chemically prepared polypyrrole. After extraction with chloroform, the FTIR spectrum has changed dramatically and looks nearly identical with that of a neat film of polypyrrole. The weak methylene stretching vibrations located between 2800 and 3000 cm^{-1} in the spectrum of the extracted film are due to residual 3ODOP molecules still trapped within the polymer film. Also note that both the chemically prepared

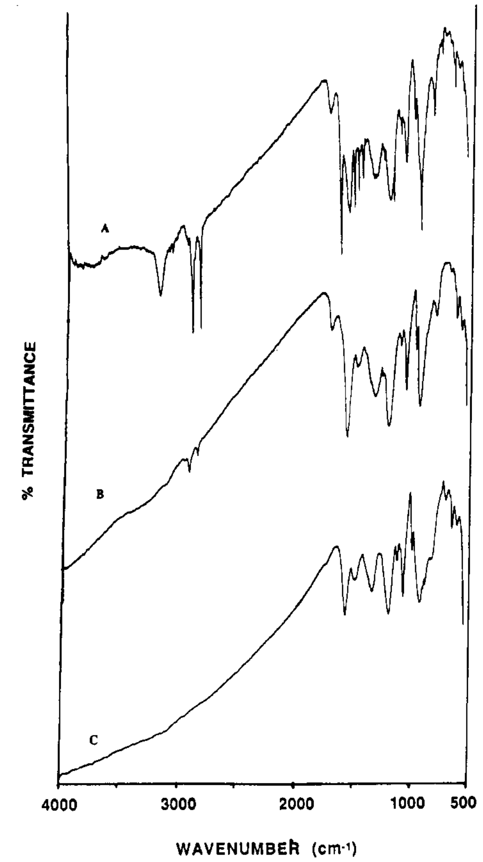

Figure 6. FTIR spectra of films prepared from a 5000/1 mole ratio of pyrrole/3ODOP spread onto a subphase containing 1% ferric chloride (A), after extraction with chloroform (B), and of polypyrrole prepared in bulk (C).

Table I. Reactions of Substituted Pyrroles and/or Pyrrole at the Air–Water Interface and Properties of Their Multilayers

spreading solution	chem reaction	electric conductivity, S/cm	thickness[a] per layer, Å
pure pyrrole	no reaction	*b*	*b*
pyrrole/$CHCl_3$	no reaction	*b*	*b*
pyrrole/stearic acid/$CHCl_3$	no reaction	*b*	*b*
alkyl- or acylpyrrole/$CHCl_3$	insulating monolayer	$<10^{-8}$	27–30
alkylpyrrole/pyrrole (1/5000)	conducting copolymer	10^{-3}–10^{-2}	100–200
acylpyrrole/pyrrole (1/5000)	conducting homopolymer	10^{-2}–10^{-1}	30–50
acylpyrrole/pyrrole/$CHCl_3$	conducting homopolymer	10^{-4}–10^{-3}	28–35

[a] Thicknesses determined by Dektak measurements. [b] No multilayer fabrication possible.

film and the LB prepared film (after extraction) exhibit a broad absorption tail that extends from about 1800 cm^{-1} into the near infrared region. This very broad, poorly defined absorption is the tail of the bipolaron band observed in the near infrared region and is a well-known signature of electrical conductivity in polypyrroles. These results clearly indicate that 3ODOP has not reacted to form copolymer (it retains its high solubility in chloroform) and that a significant amount of electrically conductive polypyrrole is formed only at the air–water interface from spreading solutions that contain a 5000/1 molar ratio of pyrrole/3ODOP.

The advantage of suppressing the reaction between the surface-active pyrrole monomer and pyrrole is revealed when one attempts to transfer the resultant surface films. For example, monolayers formed from the 5000/1 pyrrole/3ODOP system are flexible enough to be readily transferred into multilayer thin films by using the standard vertical lifting method. This in in sharp contrast to the pyrrole/3ODP system, which due to excessive film rigidity can be transferred only with some difficulty via the horizontal technique. For the 3ODOP-based system, electrically conductive monolayers are also obtained only when the mole ratio of pyrrole to surface-active pyrrole is about 5000/1. The in-plane conductivities of multilayer thin films (containing 60 layers) are typically between 10^{-2} and 10^{-1} S/cm. In addition, the measured average thickness per monolayer is about 30 Å for films created from solutions using chloroform as the carrier solvent and about 40 Å for films created from solutions utilizing pure pyrrole as the solvent. These values for monolayer thickness are much closer to the value expected for a monolayer of 3ODOP. Thus, by inhibition of the copolymerization reaction, it is possible to form flexible, electrically conductive monolayers comprised of polypyrrole homopolymer dispersed throughout a matrix of unreacted 3ODOP. In this case, the thickness of the resultant surface film is essentially determined by the dimensions of a monolayer of the surface active component. Table I summarizes the various reactions carried out at the air–water interface and lists the conductivities and thicknesses per layer obtained from the respective multilayer thin films.

The polymer film prepared from a solution of 5000/1 pyrrole/3ODOP forms a stable monolayer which, as mentioned above, is flexible enough that the vertical dipping method can be used in the fabrication of multilayer thin films. Multilayers with as many as 90 layers have been successfully fabricated. The as-prepared LB films with greater than 60 layers, however, are sometimes streaky and exhibit regions of different optical density. This effect, however, was traced to a poor deposition of the monolayers onto the back side of the substrate. Once the monolayers deposited onto the back side of the substrate (the side facing the floating barrier of the trough during the deposition process) were removed, the LB film becomes very uniform. Poor deposition to the back side of the substrate also results in deposition ratios that slowly decrease from unity as more monolayers are deposited on the substrate. To verify that deposition to the front side of the substrate was reproducible and produced uniform films, multilayers were fabricated onto glass slides as stepped films with variable thicknesses and the optical absorbance was measured for each thickness (after removal of the back side film). A linear relationship between optical density and the number of layers transferred was consistently obtained, thus confirming that the monolayers are reproducibly transferred into the film.

Low-angle X-ray diffraction measurements of multilayer thin films fabricated from the pyrrole/3ODOP system reveal only weak, poorly defined reflections that cannot be easily fit to Bragg's law to determine layer spacings. One would therefore assume that the LB films are disordered, consisting of randomly organized polypyrrole chains and 3ODOP molecules. Measurements of the conductivity across the film thickness, however, show that the multilayer thin films prepared from 3ODOP/pyrrole are highly anisotropic. The transverse conductivity of the 3ODOP/polypyrrole multilayer films is less than 10^{-9} S/cm, whereas the in-plane conductivity is typically about 10^{-2} S/cm. This represents a conductivity anisotropy $\sigma_{\parallel}/\sigma_{\perp}$ of over 10^7, which implies that the molecular organization of the LB film is also anisotropic. It is possible that the polypyrrole chains have become sandwiched between the hydrophilic planes of 3ODOP molecules during the transfer process. In such an arrangement, the extended polypyrrole chains would form continuous or near continuous layers sandwiched between 3ODOP molecules. The hydrocarbon tails of the 3ODOP molecules would then act as insulating barriers to conduction across the film but not inhibit conduction within the plane of the film. The small difference in limiting area observed at the air–water interface between monolayers of pure 3ODOP and monolayers of pyrrole/3ODOP also suggests that the polypyrrole molecules are not all contained within the condensed monolayer of 3ODOP molecules but are lying below the monolayer. In addition, reflection/absorption FTIR studies[12] clearly show that the 3ODOP molecules retain a high level of orientation within the multilayers of the mixed polymer film and that the rings of the polypyrrole chains are oriented essentially parallel to the substrate. All of these observations are consistent with the proposed molecular organization. More work is needed to confirm this structure.

The ability to construct LB films from electrically conductive polypyrroles opens the door to the fabrication of a number of new thin-film structures with novel molecular architectures and superstructures. To enhance the conductivity anisotropy of the polypyrrole LB films and to study the influence of molecular organization on their electrical properties, organic superlattices comprised of layers of electrically conductive polypyrrole/3ODOP alternating with layers of electrically insulating 3ODP monomer were fabricated. To accomplish this, bilayers of polypyrrole/3ODOP (5000/1) and 3ODP monomer were alternately transferred onto either glass slides or platinum-coated glass slides by using two LB troughs operating simultaneously. The transfer ratios of the monomer onto polymer layer and polymer onto monomer layer were both close to unity, indicating excellent transfer of both components. In fact, the polymer monolayers transfer much better onto a bilayer of the 3ODP monomer than they do onto their own bilayers (the back side transfer is close to ideal). Superlattice structures containing up to 20 bilayers of each component were easily fabricated into stepped LB films.

The in-plane conductivities of these new superlattice films are as high as 10^{-1} S/cm, whereas the transverse conductivity is less than 10^{-11} S/cm. The conductivity anisotropy of these superlattice films is therefore greater than 10^{10} and at least 3 orders of magnitude greater than the multilayers fabricated directly from polypyrrole/3ODOP. A forthcoming publication will describe in detail the temperature and frequency dependence of the electrical properties (dielectric constant, ac conductivity, etc.) of these new multilayer and superlattice LB films.

Conclusions

Two polymerization schemes have been identified that can be used to form electrically conductive polypyrroles at the air–water interface of an LB trough. Both methods are based on the spreading of a solution containing pyrrole monomer and a surface-active pyrrole derivative (mole ratio 5000/1) onto a subphase containing a suitable oxidizing agent. In one case, the surface-active pyrrole derivative (3ODP) is capable of copolymerizing with the added pyrrole, whereas in the other, the surface-active pyrrole derivative (3ODOP) serves only to promote the formation of polypyrrole homopolymer. The former system creates relatively thick surface films of polypyrrole-rich polymer that are very difficult to transfer into LB multilayer thin films. The latter system, on the other hand, produces uniform monolayer films at the air–water interface that can be readily transferred into multilayers by using a conventional vertical lifting technique.

The conductivities of the resultant multilayer thin films reach values as high as 10^{-1} S/cm. For the pyrrole/3ODOP system, the conductivity was found to be highly anisotropic with a conductivity in the plane of the film being at least 10^7 times greater than the conductivity across the film thickness. This anisotropy could be further enhanced by the formation of alternate layer structures comprised of insulating bilayers of 3ODP alternating with electrically conductive bilayers of polypyrrole/3ODOP. Thus, it is now possible to fabricate ultrathin films of conducting polymers with supermolecular organizations that can be controlled by suitable LB manipulation techniques.

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