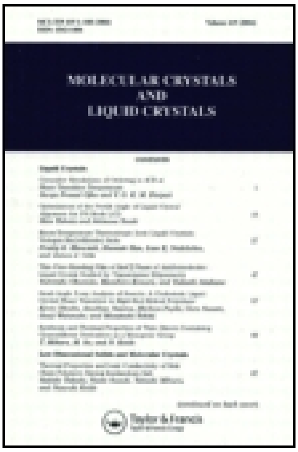

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Orientational Effects in 3-*n*-Hexadecylpyrrole Langmuir–Blodgett films

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3-*n*-hexadecylpyrrole have been synthesized, and Langmuir–Blodgett films of this compound have been studied by means of transmission and grazing incident reflection FT-IR spectroscopy. A comparison of the spectra at the two different polarizations shows that the hydrocarbon tails are oriented normal to the substrate surface for multilayer LB films. For the single monolayer LB films, the hydrocarbon tails are tilted with respect to the substrate surface possibly due to interactions between the pyrrole head groups and the platinum substrate.

INTRODUCTION

Mono- and multilayer structures assembled on a water surface and subsequently transferred to a substrate provide a rational approach for fabricating interfaces with a well defined composition, structure and thickness. Such assemblies are attractive model systems for elucidating the relationship between structure and function for a variety of heterogeneous phenomena, including catalysis, corrosion, lubrication, and adhesion. Interest in these two-dimensional systems has grown considerably because of their potential use as synthetic mem-

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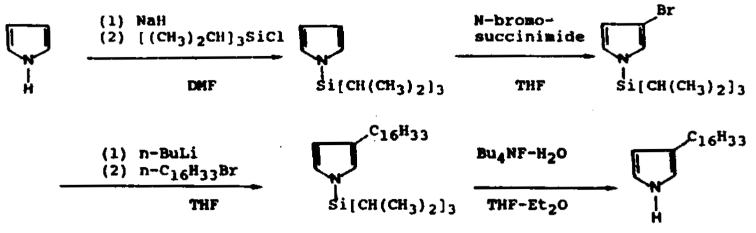
branes, nonlinear optical systems, sensors, and microelectronic devices. Coupling Langmuir–Blodgett techniques with electroactive polymers opens new possibilities for design of optically and electrically active interfaces.

Here we present the first study of the Langmuir–Blodgett film with pyrrole as head groups. The pyrrole head groups could be polymerized by adding $FeCl_3$ to the aqueous subphase. The detailed study of the polymerization will appear in a subsequent publication. In this paper, we will discuss the LB films of $C_{16}H_{33}$-pyrrole monomer only. Numerous studies have been conducted of LB films to determine the structure and orientation of the films.[1-4] In this paper we report the infrared reflection absorption spectroscopy (IRRAS) study of pyrrole LB films. A detailed description of the IRRAS technique can be found elsewhere.[5-7] When light is reflected from a flat metal surface, the component polarized perpendicular to the plane of reflection (the plane which contains both the incident and the reflected beams and is perpendicular to the metal surface) undergoes a phase shift of about 180 degrees at virtually all angles of incidence, and hence, the reflected beam will destructively interfere with the incident beam, producing a node at the reflective surface. The component polarized parallel to the plane of reflection experience a phase shift on reflection varying from zero degrees at small incident angles to about 180 degrees at large angles. For grazing incident angle, the net result is an electric field vector polarized normal to the reflecting metal surface. With grazing incident angle, only the vibrational modes with a component of the dipole transition moment oriented along the surface normal will be excited. On the other hand, only those vibrational modes with a component of the dipole moment parallel to the substrate can be detected by transmission measurements. From comparing these two spectra, it is possible to study the orientation of the well characterized functional groups. These surface selection rules and the sensitivity to study monolayer on metal surfaces make FTIR an ideal tool for investigating the orientational effects of LB films.

EXPERIMENTAL

Synthesis of the 3-*n*-hexadecylpyrrole was carried out with a procedure similar to that used by Muchowski *et al.*[9,10] The procedure is shown in Scheme 1.

The LB films were prepared on a modified commercially available Lauda film balance. The schematic diagram of the LB film formation is shown in Figure 1. The subphase was purified water with 0.57 mg/



SCHEME 1 Procedure for $C_{16}H_{33}$-Pyrrole monomer synthesis

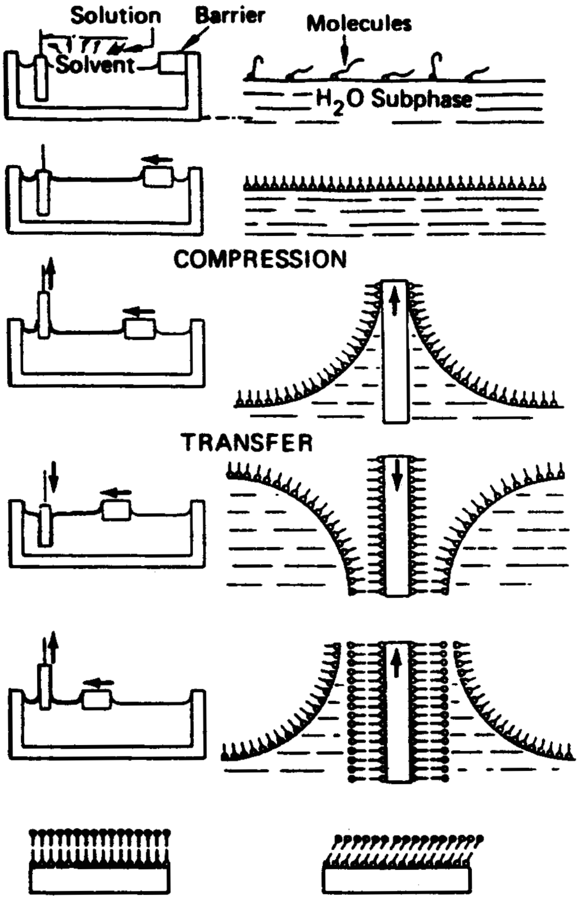


FIGURE 1 Schematic diagram of the Langmuir-Blodgett film formation and deposition.

2ml $C_{16}H_{33}$-pyrrole and 0.98 mM $CHCl_3$. The surface pressure isotherm is shown in Figure 2. The monolayers were transferred to substrate at a pressure of 20 mN/m. The substrate were ZnSe crystals and Si wafers for transmission, and platinum coated microscope slides for reflection. The sharp rise of pressure in Figure 2 indicates a good quality LB film.

The FTIR spectra were taken with a Mattson Cygnus 100 with room temperature DTGS detector for reflection, and a liquid nitrogen cooled MCT detector for transmission. For studying the orientation of the pyrrole LB films, the C-H and N-H stretching modes are the most appropriate signatures. The assignment of these bands are listed in Table I. Figure 3 shows that the transmission and IRRAS spectra for a spin coated $C_{16}H_{33}$-Pyrrole film. The similarity of these two spectra indicate the functional groups are randomly oriented. Figure 4 gives the transmission spectrum (A) and IRRAS spectrum (B) of five monolayers and IRRAS spectrum of one monolayer (C) LB film. For the five monolayer LB film, the N-H stretching mode, with dipole moment nearly parallel to the hydrocarbon tail, appears in the reflection spectrum with about 10 cm^{-1} shift to lower wavenumbers compared with the spin coated film. The N-H stretching mode completely disappears in the transmission spectrum.

The polarization dependent intensity change of the 2962, 2954 and

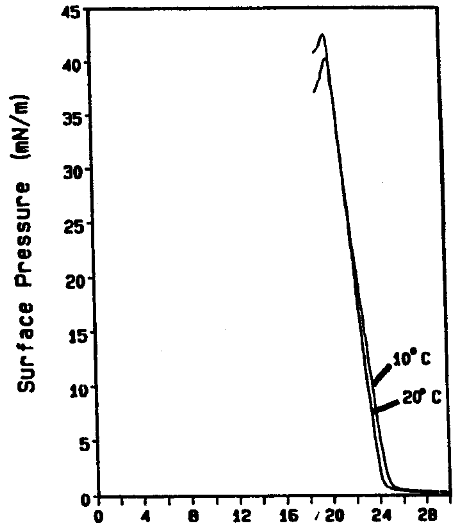


FIGURE 2 Isotherm of $C_{16}H_{33}$-Pyrrole

TABLE I

Band Assignment for $C_{16}H_{33}$-pyrrole LB film in the Wavenumber Range 3200 to 2800 cm^{-1}

Frequency cm^{-1}	Mode	Polarization relative to the hydrocarbon tails
3367	ν (NH)	parallel
2962	$\nu_a(CH_3)$ in skeletal plane	parallel
2954	$\nu_a(CH_3)$ out of skeletal plane	perpendicular
2920	$\nu_a(CH_2)$	both
2875	$\nu_s(CH_3)$	parallel
2853	$\nu_s(CH_2)$	both

ν Stretch (a, asymmetric; s, symmetric)

2875 cm^{-1} C-H stretching modes are highlighted in Figure 5. The dipole moment of the CH_3 asymmetric stretching mode (in the skeletal plane) at 2962 cm^{-1} and the CH_3 symmetric stretching mode at 2875 cm^{-1} are parallel to the hydrocarbon tail, while the dipole moment of the CH_3 asymmetric stretching mode (out of the skeletal

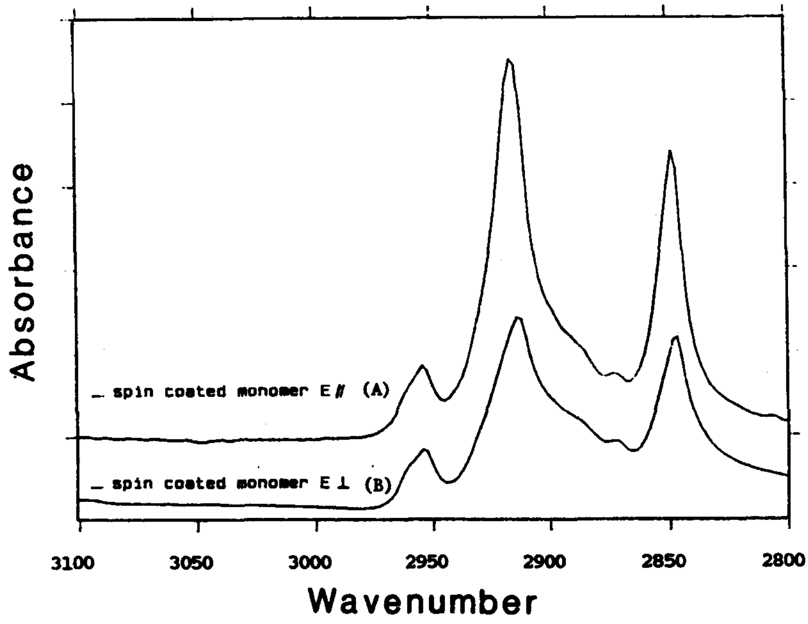


FIGURE 3 FTIR spectra of spin coated $C_{16}H_{33}$-Pyrrole monomer films: (a) Transmission of spin coated film on Si substrate; (b) IRRAS of spin coated film on Pt substrate.

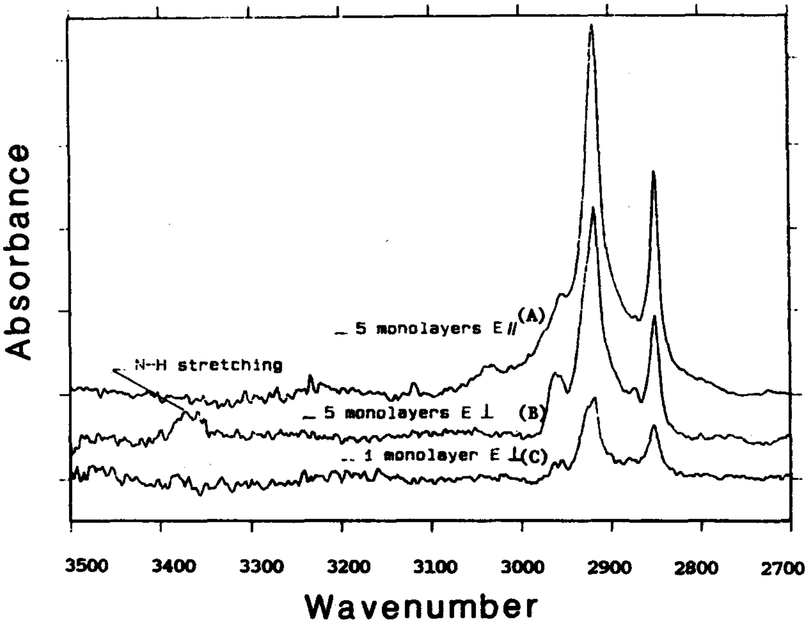


FIGURE 4 FTIR spectra of $C_{16}H_{33}$-pyrrole LB films in the C—H and N—H stretching region: (a) Transmission of 5 monolayers on ZnSe; (b) IRRAS of 5 monolayers on Pt; (c) IRRAS of 1 monolayer on Pt.

plane) at 2954 cm^{-1} is perpendicular to the hydrocarbon tail. By comparing the spectra (A) and (B), in Figure 5, it is apparent that the intensities of the 2962 cm^{-1} and 2875 cm^{-1} modes are considerably diminished in (A), where the electric field vector is parallel to the substrate. This suggests that the CH_3 end group is oriented approximately normal to the substrate, which implies a similar orientation of the hydrocarbon tail. This is consistent with the disappearance of the N-H stretching mode in the transmission spectrum.

The relative intensities of the 2962, 2954 and 2875 cm^{-1} peaks in spectrum (C) are in-between those of (A) and (B). As can be seen from Figure 5, the 2962 cm^{-1} peak is the dominant feature whereas the 2954 cm^{-1} peak is weaker in spectrum (B). In spectrum (A), the relationship is inverted, and the two peaks have approximately the same intensity in spectrum (C). This would imply that the single monolayer LB film on platinum is oriented with the hydrocarbon tails tilted at an angle to the substrate normal. This could be due to the interaction between the π-electron cloud of the heterocyclic ring of the head group and the platinum substrate as observed by EELS[10]

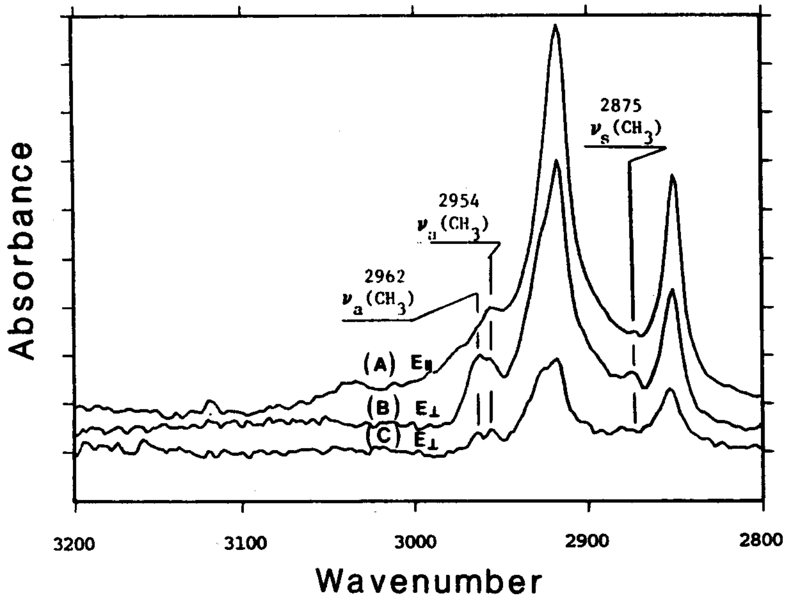


FIGURE 5 FTIR spectra of $C_{16}H_{33}$-pyrrole LB films in the C—H stretching region: (a) Transmission of 5 monolayers on ZnSe; (b) IRRAS of 5 monolayers on Pt; (c) IRRAS of 1 monolayer on Pt.

for pyrrole monomers adsorbed on Pt substrate and by NEXAFS[11] for poly(3-methylthiophene) electrochemically grafted on a Pt electrode. The schematic diagram of the orientation of $C_{16}H_{33}$-Pyrrole five monolayers and one monolayer on Pt substrate is shown in Figure 6.

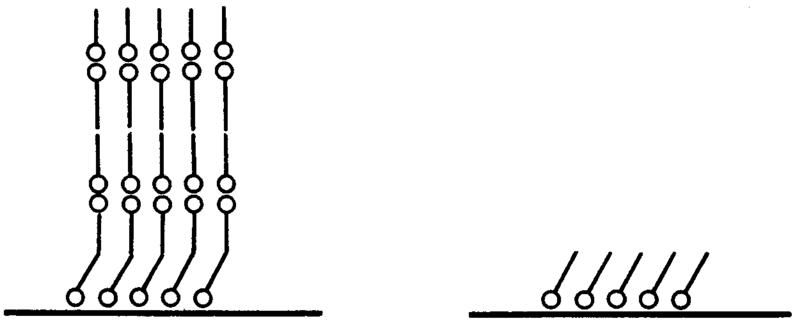


FIGURE 6 Schematic diagram of the orientation of $C_{16}H_{33}$-pyrrole LB films with five monolayers and a single monolayer.

CONCLUSION

We have demonstrated that stable monolayers of 3-*n*-hexadecylpyrrole may be formed on a water subphase and transferred to a solid substrate by means of the Langmuir–Blodgett technique. Infrared spectroscopy shows that the hydrocarbon tails are oriented normal to the substrate for multilayers, while for single monolayer on a Pt substrate, the tails are tilted relative to the surface. This might be due to the interaction between the π-electron of the pyrrole ring in the head group and the Pt substrate.

Acknowledgments

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