Mesogenic Pyrrole Derivatives in Langmuir-Blodgett Films

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A pyrrole monomer linked through a spacer of various lengths (0, 3, or 8 carbons) to a mesogenic core has been studied in Langmuir and Langmuir–Blodgett (LB) films. Pure monolayers of these mesogenic pyrrole derivatives have been transferred onto solid substrates, leading to highly ordered built-up films. The spacer between the mesogenic core and the pyrrole moiety has clearly no influence on the organization of these molecules in the LB films. These multilayers can be easily polymerized and oxidized by iodine vapors. As shown by GPC analysis, the obtained polymers have a variable molecular weight depending on the spacer length. Alternated layers of one of these pyrrole derivatives and 1-monostearoyl-*rac*-glycerol lead to similar results for the polymerization, suggesting that this reaction occurs mainly in each monolayer and not between two successive layers. Conductivity of the obtained material is highly anisotropic: about $10^{-1}-10^{-2}$ S·cm⁻¹ for the in-plane conductivity and less than 10^{-8} S·cm⁻¹ for the conductivity across the film. No correlation has been found between the conductivity of the LB films and the length of the polymers: conductivity of such material is then mainly limited by defects in the LB films and poor conductivity between molecules.

Introduction

Langmuir-Blodgett (LB) technique allows one to organize molecules into thin films with a well-defined thickness. The particular structure of these LB films explains the considerable attention received by this technique to elaborate new materials with specific chemical or physical properties. In particular, studies of electrical conductivity for such highly ordered systems have been the goal of a large amount of works, which are based on electroactive molecules¹ or electroactive polymers. A large variety of conducting polymers has been utilized with the LB technique leading to anisotropic conducting material. The corresponding monomers were mainly derivatives of thiophene,² aniline,³ or pyrrole. Alkyl chains of various lengths were then attached to the pyrrole cycle directly^{4,5} or through ketone⁵ or carboxylic group leading to amphiphilic compounds suitable for Langmuir studies.^{4,6} However, these pyrrole derivatives need to be mixed with some other molecules to lead to a successful transfer onto solid substrate and a good polymerization of the pyrrole moieties. For example, Hong et al. has developed a synthesis of a conductive polypyrrole formed by spreading a surface-active pyrrole together with unsubstituted pyrrole (mole ratio ca. 1/5000) onto a subphase containing ferric chloride.⁷ Depending on the structure of the surface-active pyrrole, the obtained polymer contains no or a few percentages of this pyrrole derivative. This polymer could be then considered as mainly poly(unsubstituted pyrrole). Other pyrrole derivatives⁶ have been studied in LB films by Shimidzu *et al.* Using a mixture of the surface-active pyrrole with octadecane (ratio 2/1), they were able to transfer films from the air-water interface onto solid substrate and then to polymerize the builtup films by electrochemistry with some predissolution of the LB films in acetonitrile.

Using a mixture instead of a pure compound is a clear limit of such system. To improve the behavior in Langmuir and Langmuir-Blodgett films of such derivative, one should change their chemical structure in such way that high organization of



StGly

Figure 1. Molecular structure of compounds used in this work.

pure films could be achieved together with some relative flexibility of the pyrrole moiety to allow them to polymerize easily.

Recent studies⁸ have shown that mesogenic groups can be used instead of simple alkyl chains for new derivatives having good Langmuir and Langmuir–Blodgett properties. Calamitic mesogenic groups appear attractive for LB studies because they could lead to nematic or smectic phases which are somewhat compatible with the lamellar structure of the LB films.

In this paper, we describe the behavior of new pyrrole derivatives (see Figure 1 for their molecular structure) in

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TABLE 1: Phase Transition in Bulk and in Langmuir Film of the C_nC₈ Monomers



^a [] denotes monotropic transition.

Langmuir and Langmuir-Blodgett films. These monomers C_0C_8 and C_nC_8 (namely 4-octyloxy-4'-(alkyloxy)phenylbenzoate-3-pyrrolylacetate) are based on a pyrrole ring linked to a mesogenic core (i.e., a phenylbenzoate group) through a spacer of various lengths. In bulk, they exhibit monotropic smectic A phases described in Table 1. Characterization of the molecular organization in the LB films has been done by different techniques including infrared dichroism and X-ray diffraction. To our knowledge, the polymerization (by iodine vapors) and analyses by GPC of the resulting polymers were attempted for the first time on such LB systems. Through these experiments, we point out the influence of the mesogenic group and of the spacer length on the properties and the polymerization of such LB films.

Experimental Section

The synthesis of the pyrrole derivatives C_3C_8 and C_8C_8 is described elsewhere.⁹ The PyC₁₈ compound was obtained in a similar way. C_0C_8 was synthetized with the following procedure: 12.5 g (25 mmol) of 4-octyloxybenzoic acid is dissolved in 40 mL of thionyl chloride. After 2 h of reflux, the SOCl₂ excess is evaporated; 40 mL of pyridine and 16.5 g (0.15 mol) of hydroquinone are then added. After 2 days of stirring at room temperature, 20 mL of hydrochloride acid mixed with ice is poured in the solution. The product is extracted with petroleum ether and washed with water until pH neutrality is reached. Purification on silica column (eluent heptane/ether 5/5) leads to the pure HOC₈. Coupling reaction between HOC₈ and the pyrrole moiety is already described in ref 9. The ultimate purifications were done by chromatography or HPLC and the purities of the products were checked by TLC and ¹H NMR. All monomers gave correct elemental analysis: Found for C₀C₈: C 71.71%, H 7.08%, N 2.93%, O 17.22%; Calculated: C 72.14%, H 6.95%, N 3.12%, O 17.79%. The glycol derivative StGly (namely 1-monostearoyl-rac-glycerol) was obtained from Sigma (purity 99%) and was used without further purification.

The compression isotherm curves were recorded using a home-made Teflon trough, working at different temperatures and under a continuous nitrogen flow saturated with water. The surface pressure was measured by a Wilhelmy balance using a probe made of a single strip of filter paper. The subphase was Millipore Q-grade water with a resistivity higher than 18 MQ·cm. Chloroform (HPLC grade from Prolabo) was used as spreading solvent and the solutions (concentration ca. 10^{-3} M) were stored at -18 °C between experiments to limit solvent evaporation and degradation of the pyrrole derivative.

Built-up films have been obtained by the vertical lifting method using a large-area ATEMETA trough¹⁰ working at room temperature under a continuous dried nitrogen flow. A stepwise compression was performed to reach the transfer surface pressure. Dipping speed was generally set to 2 cm/min. Films were deposited onto optically polished calcium fluoride or zinc selenide for infrared linear measurements and onto optically polished glass substrate for low-angle X-ray experiments.

Alternated LB films were obtained with an alternate KSV 5000 trough at room temperature and under a continuous nitrogen flow saturated with water. The substrate went down through a 1-monostearoyl-*rac*-glycerol monolayer with a dipping speed of 1 cm/min and came up through a C_3C_8 monolayer with the same speed. Before the next deposition cycle, the film was dried during 5 min.

Infrared spectra were recorded on a FTIR 750 Nicolet spectrometer. IR linear dichroism was performed to calculate the dichroic ratio R:

$$R = A(i=60^{\circ})/A(i=0^{\circ})$$
(1)

where A(i) is the absorption coefficient and i the angle between the plane of the LB film and the IR light electric vector. This ratio R is related to the degree of anisotropy out of the substrate plane and allows one to estimate the angle ϕ between the normal to the substrate and the dipole moment of a particular vibration with a precision of few degrees. All the assumptions made for these calculations are given elsewhere.¹¹

X-ray diffraction experiments ($\theta - 2\theta$ scans) were performed with an apparatus previously described.¹²

A UV detector (Varian 2550) working at a wavelength of 254 nm combined with a Varian HPLC 2510 pump and TSK gel columns (G3000H8, G2000H8, and G1000H8) was used for GPC analysis. The flow rate of THF eluent was set to 0.7 mL/min. The LB film sample was dissolved in ca. 300 μ L of THF and 100 μ L of this solution was injected for analysis. Mean molar masses \bar{M}_n and \bar{M}_w were then calculated using polystyrene standard calibration.

DC conductivity measurements were performed with a Keithley Model 617 electrometer. For in-plane measurements, two electrodes were in contact with the LB films by silver Electrodag from Acheson. The conductivity of the material was deduced from the resistance between these two electrodes and the thickness of the films. For conductivity across the multilayers, the method employed is described in ref 6 and uses silated ITO electrodes as substrate. For both measurements, the thickness of the multilayers was estimated from the interlayer spacing obtained by X-ray diffraction and the number of layers transferred onto the substrate.

Results and Discussion

1. Isotherms at the Nitrogen-Water Interface. The surface pressure/molecular area isotherms of the different molecules used in this study were recorded to evaluate the molecular packing in the monolayers and to point out phase transitions which could take place in the film during compression.

Figure 2 gives the isotherms of HOC_8 for two different temperatures. As one can see, a plateau in the surface pressure (close to 15 mN/m) is the main feature of the compression isotherm obtained at low temperature (i.e., 5 °C). This could be related to a phase transition of the monolayer from an expanded liquid phase to a condensed liquid phase. As expected



Figure 2. Isotherm of HOC₈ on pure water obtained with a constant compression speed of ca. 1.8 Å²/molecule/min at 20 °C (O) and 5 °C (\bullet).



Figure 3. Isotherm of C_0C_8 on pure water obtained with a constant compression speed of ca. 1.8 Å²/molecule/min at 20 °C (O) and 4 °C (\bullet).

in such case, the phase transition disappears when the subphase temperature is increased (see Figure 2). The C_0C_8 molecule which differs from HOC_8 just by the pyrrole moiety shows the same kind of behavior at the nitrogen-water interface. Indeed, a phase transition appears at low temperature for this monolayer (see Figure 3 and Table 1). Even if the range of temperature in which this phase transition is observed is not exactly the same for HOC₈ and C_0C_8 , the similarities in the behavior of those two molecules show that the properties of C_0C_8 are still highly induced by the mesogenic group despite the presence of the pyrrole moiety in this molecule. On the contrary, no phase transition could be observed for C_3C_8 and C_8C_8 monolayers in the temperature range 4-30 °C. This indicates that the spacer between the mesogenic group and the pyrrole moiety has some influence in the final properties of the C_nC_8 molecules. This hypothesis is confirmed when one compares the isotherms of the different molecules at a same temperature in their expanded liquid phases (see Figure 4). When the spacer length is increased, the isotherm of the pyrrole derivative undergoes a shift from the one of C_0C_8 to the one of PyC_{18} . The C_8C_8 molecule has a surface pressure/molecular area curve very close to PyC_{18} , suggesting that the long spacer of C_8C_8 gives to this compound a behavior close to an alkyl chain derivative. Overall, the mesogenic group introduced in the nonpolar part of the pyrrole derivative has a strong influence on the interfacial properties of the molecule when the spacer is short or null and its influence is highly decreased when the spacer is long.

2. Langmuir-Blodgett Films. The pure monolayer of a C_nC_8 monomer is easily deposited onto hydrophilic or hydrophobic substrates for a surface pressure around 25-30 mN/m.





Figure 4. Isotherms of C_0C_8 (\bigcirc), C_3C_8 (\square), C_8C_8 (\blacksquare), and PyC₁₈ (\bigcirc) on pure water obtained with a constant compression speed of ca. 1.8 Å²/molecule/min at 20 °C.



Figure 5. Infrared spectra of 49 layers of HOC₈ deposited on calcium fluoride. The angle between the plane of the substrate and the electric field is either 0° or 60° . For clarity, the origin of the second spectrum is shifted.

The resulting Y-type LB films are light diffusing, which could be due to a polycrystalline structure. The transfer ratio is found in the range 0.9-0.7 depending on the molecule used. This value lower than unity could correspond to some tilting process during the transfer from the water surface onto the solid substrate. This is indeed confirmed by infra-red and X-ray experiments.

Infrared Measurements. To characterize the organization of these C_nC_8 molecules in the LB films, infrared dichroism is one of the techniques leading to the evaluation of orientations of different parts of molecules within the LB films. Figure 5 gives as an example the spectra of a HOC₈ LB film for two different orientations of the substrate relative to the IR beam. Large differences in the intensities of various peaks could be observed and are related to the orientations of the molecule. More precisely, the two broad peaks at 3444 and 3360 cm^{-1} are related to the stretching mode of the OH function. The presence of two bands instead of a single one may indicate various surroundings (probably, changes in hydrogen-bond network) for the hydroxyl group of HOC₈ in multilayers. As deduced from the IR dichroism experiments (see experimental part for details), one set of OH is mainly oriented at 37° relatively to the normal of the substrate when the other set presents no particular orientation. The bands in the 2800-3000 cm⁻¹ region associated to the stretching of CH bonds characterize the alkyl chains, which are supposed to adopt a fully extended all-trans conformation in the LB film. Their dichroic ratios suggest that the dipole moment of these vibrations is



SUBSTRATE

Figure 6. Average orientation of the C_nC_8 molecules in the LB films as deduced from infrared dichroism.

TABLE 2: Analysis of the IR Dichroism for the C_nC_8 LB Films

C_0C_8	$\overline{\nu}$ (cm ⁻¹)	3400	3371	2930	2850	1609	1512
	mode	$\nu_{\rm NH}$	$\nu_{\rm NH}$	$\nu_{\rm CH_2}$ as	VCH ₂ s	ν_{8a}	V19a
	Φ (deg)	58	60	59	59	46	47
C_3C_8	$\bar{\nu}$ (cm ⁻¹)	3400	-	2928	2850	1609	1512
	mode	$\nu_{\rm NH}$	-	VCH2 as	VCH ₂ s	ν_{8a}	v_{19a}
	Φ (deg)	59	_	58	59	49	42
C_8C_8	$\bar{\nu}$ (cm ⁻¹)	3410	-	2917	2850	1608	1513
	mode	$\nu_{\rm NH}$	-	VCH2 as	VCH2 s	ν_{8a}	v_{19a}
	Φ (deg)	60	-	58	60	47	45

oriented near 59° with respect to the substrate normal. Since these dipoles of CH₂ vibrations are perpendicular to the hydrocarbon chain axis,¹³ one could conclude that the hydrocarbon chain of HOC₈ is tilted in the LB films relatively to the surface with an angle value around 31°. Furthermore, two welldefined peaks at 1609 and 1514 cm⁻¹ could be related to the vibration modes ν_{8a} and ν_{19a} of the 1,4-disubstituted benzene rings¹⁴ of the mesogenic core. The associated transition dipole moments are mainly parallel to the substitution axis of these rings, axis which are close to the main direction of the phenylbenzoate group.¹⁵ These bands give then the average orientation of the mesogenic core in the LB multilayers. From the experimental data, one found a tilting angle ϕ around 25°– 30°. The IR dichroism suggests then that the mesogenic part of HOC₈ is tilted with the same angle than the alkyl chain.

Using the same approach for the C_nC_8 series, one could record the IR spectra of the built-up films. As expected, all of these spectra are very similar, except the one of C_0C_8 which presents in particular two NH bands. This phenomenon already observed for HOC₈ could be induced by hydrogen bonding between molecules inside the multilayers. From these spectra, one could calculate the tilting angle associated with various vibrations of these pyrrole derivatives (see Table 2). Very close orientations are found for the different parts of these molecules. This proves that the spacer has only a small influence on the organization in LB films. More precisely, one can see in Table 2 that a large tilt angle ($\phi \approx 60^\circ$) corresponds to the NH vibration ($\nu =$ 3400 cm^{-1}). The pyrrole group is highly tilted in the multilayer. This result is quite similar to experimental data obtained for polypyrrole/3-octadecanoyl pyrrole LB films,16 for which Cheung et al. suggested that the substituted pyrrole ring is lying approximately parallel to the substrate plane. From the bands at 1609 and 1512 cm⁻¹, the orientation of the mesogenic core is evaluated: its tilt angle is close to $45^{\circ} \pm 5^{\circ}$. Furthermore, the average tilting of the alkyl chains is found near 30° with respect to the normal of the substrate. The common orientation of C_nC_8 deduced from these infrared measurements is illustrated by Figure 6.

Further evidence for the average tilt of the pyrrole derivatives in LB films is given by X-ray diffraction.

X-ray Diffraction. The experiments were mainly done on the C_3C_8 built-up film with a number of layers equal to 49.



Figure 7. X-ray diffractogram of 49 layers of C_3C_8 deposited onto a glass substrate. The diffracted intensity *I* is expressed in arbitrary units and the momentum transfer *Q* in Å⁻¹.



Figure 8. Infrared spectrum of 49 layers of C₈C₈ deposited on calcium fluoride, before and after polymerization by iodine vapors.

Figure 7 shows a part of the θ -2 θ diffractogram for such LB film. The high number of reflexes shows that the lamellar structure is perfectly well-defined. However, the large periodicity of 121.0 ± 1.0 Å for these LB films was a puzzling fact. Indeed, the pyrrole C_3C_8 in its smectic A phase is characterized by a layer thickness of 35 Å,⁹ a distance which is consistent with the length (35.5 Å) of the molecule C₃C₈ evaluated with a CPK model. The periodicity found in LB films corresponds then to about four layers of pyrrole C₃C₈, instead of the two expected for Y-type LB films. This kind of phenomenon has already been observed for liquid-crystalline discotic compounds in bulk and in LB films¹⁷ and was interpreted by positional distortion between bilayers. This unusual periodicity and the high number of observed Bragg peaks clearly indicate the influence of the mesogenic group to well organize compounds in the multilayers. Anyway, the deduced thickness for one layer of pyrrole C₃C₈ is then 30.3 Å, a value smaller than the layer thickness of the mesogenic pyrrole in its smectic A phase. This comparison indicates again the tilting of the pyrrole C3C8 in the LB film, a tilt which can be evaluated from these X-ray data to ca. 30° with respect to the normal of the substrate. Further studies are in progress for the other pyrrole derivatives described in this work.

2. Polymerization of the LB Films. The built-up films of C_nC_8 were exposed to iodine vapors at room temperature during typically 30 min. After exposure, the film color turns to deep brown and the infrared spectrum presents large changes (see Figure 8): broadening of the bands is observed for wavenumbers

TABLE 3: Polymerization of the C_nC_8 Monomers in LB Films

	C_0C_8	C ₃ C ₈	C ₈ C ₈
$\overline{\dot{M}}_{n} (g/mol)^{a}$ I^{a}	6000-12000	7000-11000	12000-25000
	1.2-2	2-5	2-100

 ${}^{a}\bar{M}_{n}, \bar{M}_{w}$, and I (equal to \bar{M}_{w}/\bar{M}_{n}) are determined by gel permeation chromatography versus polystyrene standards calibration.

lower than 2000 cm⁻¹ and a very broad and intense band is appearing around 4800 cm⁻¹. This band could be associated with an electron delocalization and means then that some polymerization process occurs in the LB film. Indeed, the effect of oxidant such as iodine and bromine on pyrrole in bulk has been described.¹⁸ These halogens induced the polymerization of pyrrole and simultaneously the oxidation of polypyrrole, leading to a conducting polymer. To our knowledge, this kind of polymerization study was never done in LB films. In fact, the previous pyrrole derivatives (except the hexadecylpyrrole) used in Langmuir or LB films had a pyrrole ring linked directly to a ketone, a structure which highly modifies the redox properties of the compound and then their polymerization. For example, the oxidation potential of 3-ethylpyrrole is 0.15 V vs. SCE, while for the 3-acetylpyrrole this potential reaches 0.9 V.¹⁹ The oxidation potential of iodine is found between these two values.²⁰ The polymerization of pyrrole C_nC_8 LB films is clearly demonstrated and analyzed by gel permeation chromatography. The chromatogram of an LB film exposed 20 min to iodine vapors exhibits a new very broad peak with diminishing or disappearance of the peak corresponding to the monomer. Clearly, the reaction is complete after less than 30 min at room temperature giving mainly short polymers or even oligomers. The analyses in term of mean molar mass and polydispersity obtained for 3-5 samples are reported in Table 3 for the C_nC_8 series. In bulk and for the C_3C_8 compound, similar mass has been observed⁹ but with an unusual polydispersity close to unity. The higher polydispersity measured in LB films is surely due to the large quantity of initiator (i.e., iodine) compared to the quantity of monomer. One important feature of this polymerization in LB films is the higher polydispersity and the slight increase in the molar mass of the obtained polymer when the spacer length is longer. Especially in the case of the C_8C_8 compound, the chromatogram reveals polymers with very high mass (explaining the increase of the polydispersity compared to C_0C_8). As shown by IR dichroism, the C_nC_8 molecules have a quite comparable organization within the LB films. The change in mean molar mass is then not induced by some modification in the pyrrole orientation but should be related to the chemical structure of each compound and in particular the spacer length. In fact, one could suppose that the spacer linking the pyrrole moiety to the mesogenic core is controlling the pyrrole ability to reach one other pyrrole for polymerization. Short spacer could lead to poor mobility of the pyrrole with respect to the rigid part of the molecule and therefore could limit the polymerization to a few numbers of monomers. On the other hand, long spacer could give to the pyrrole enough mobility to reach easily further monomer and to continue the polymerization reaction.

After polymerization, the LB organization is highly modified as shown by X-ray diffraction, where few diffraction peaks (not very well resolved) are observed corresponding to a periodicity of ca. 54.1 ± 0.4 Å. However, it is difficult to characterize from these diffractograms the order in the polymer multilayers because of the iodine excess which is still present in the polymerized film. The Y-type structure of the LB films corresponds to a bilayer organization in which pyrrole moieties of successive layers are facing each others. A priori, the polymerization could then involve either these two layers of pyrrole groups leading to zigzag polymers between two successive layers, or could be restricted to a single monolayer. Alternated LB films were then built up to decide between these two possibilities. After each pyrrole layer, one layer of nonpolymerizable compound was deposited to avoid any polymerization between two successive layers. Following different experiments, the glycerol derivative StGly was used for such study since good transfer ratios are obtained during the successive deposition of C_3C_8 and StGly. The built-up film has no optical defect, showing that the polycrystalline aspect of the pure C₃C₈ multilayers disappears when avoiding interactions between pyrrole layers. The alternated layers were then polymerized under the same conditions as the pure C₃C₈ films and analyzed by GPC. No change in the mean molar mass of the obtained polymer compared to the one in pure LB films has been observed. Other measurements like IR spectroscopy and conductivity show no clear modifications between the pure and alternated layers. These results strongly suggest that the polymerization takes place mainly in each monolayer and that cross polymerization between two successive layers, if existing, is only a minor process during the reaction.

3. Conductivity of the Polymerized LB Films. The electrical properties of the polymerized materials were measured just after the polymerization and the doping process. Indeed, the conductivity of the material dropped dramatically after few days due to instabilities of the doped polymers. For all molecules of the C_nC_8 series and for all mean molar masses of the obtained polymers, these doped LB films present an inplane conductivity of ca. $10^{-1}-10^{-2}$ S·cm⁻¹. For the out-ofplane conductivity, values between 10^{-11} and 10^{-8} S·cm⁻¹ were found in the case of the C_3C_8 derivative. This anisotropy of the conductivity is, of course, induced by the layer structure of the LB films which is not totally suppressed by the polymerization process. The noncorrelation between the mass of the polymers and the conductivity of the films indicates that the limitation to this conductivity is not the intrinsic conductivity of each polymer but the defects in the layers and the conductivity between polymers within the LB film.

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Mesogenic Pyrrole Derivatives in LB Films

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