Fabrication of Langmuir–Blodgett Films of Polypyrrole by Solid State Reactions on an Iron(III) Stearate Template

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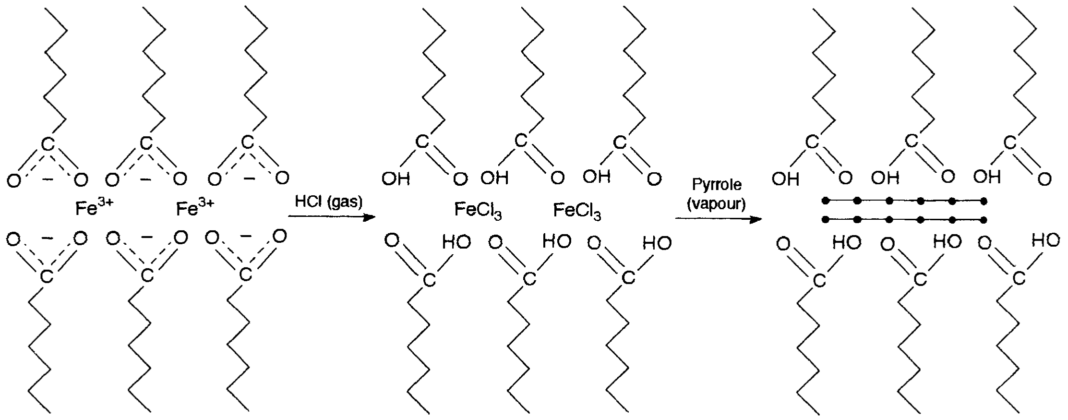
The sequential exposure of Langmuir–Blodgett films of iron(III) stearate to hydrogen chloride gas and pyrrole vapour results in the formation of doped, conductive layers of polypyrrole within the fatty acid multilayer; conductivities as high as 10 S cm^{-1} have been achieved.

The Langmuir–Blodgett (LB) technique represents one of the few methods by which organic films of controlled thickness and highly ordered structure may be deposited onto a substrate. The use of this method to deposit films of electrode-active materials shows great promise for applications in electronics and micro-devices and considerable effort has been made towards the fabrication of highly anisotropic, ultra thin, semiconducting films.[1–3] Both organic and inorganic compounds have been used for this task, however, the diversity in the properties and chemistry of conductive polymers make these materials natural candidates for LB manipulation. Polypyrroles appear particularly suited to the job because of their high conductivity and excellent environmental stability. To date, several methods for depositing LB films of polypyrrole have been developed including the electropolymerization of amphiphilic pyrrole derivatives[4] and the direct polymerization of pyrrole with a surface active derivative at the air–water interface of the trough.[5] In this paper, we present a new method that involves the modification of a preformed LB film by exposure to gaseous reactants. Solid state reactions of LB films, such as this, have the advantage of altering the chemical structure of the film without adversely affecting the molecular order.[6,7] Some attempts have been made to insert conducting or semiconducting inorganic materials by this method however the resultant precipitates manifested themselves as micro-aggregates rather than thin planes due to the high cohesive energy of the crystals.[8–10] The method proposed herein involves the precipitation of iron(III) chloride within the planes of a multilayer by exposing a LB film of iron(III) stearate to hydrogen chloride gas (see Scheme 1). The precipitated salt then acts to polymerize pyrrole and dope the resultant polypyrrole when the film is treated a second time with the vapour of this monomer. Polypyrrole, which has a relatively low cohesive energy, forms highly conductive domains within the insulating fatty acid multilayer.

The formation and deposition of iron(III) stearate monolayers have already been reported in the literature.[11] The iron(III) stearate multilayers were produced by the standard Langmuir–Blodgett vertical dipping technique by first spreading a solution of stearic acid in chloroform (1 mg ml^{-1}) onto a subphase of high purity water and iron(III) chloride ($3–12 \times 10^{-5}$ mol dm^{-3}). The resultant films were compressed to 32 mN m^{-1} producing a pressure–area isotherm closely resembling that of cadmium stearate. Slower than normal dipping rates (5–10 mm min^{-1}) and longer drying times between dips (1 h) were used to accommodate these stiffer films and prevent the deposition ratios from dropping below unity. This procedure was used to deposit between 20 and 30 layers of iron(III) stearate onto glass slides which had previously been rendered hydrophobic by chemical treatment. Infrared spectra of the slightly yellow LB films show a strong absorption of the carboxylic head groups at 1523 cm^{-1} and a smaller peak at 1685 cm^{-1} signifying that nearly all of the fatty acid had been deposited as an iron(III) salt. Weaker absorptions at 1586 and 3400 cm^{-1} suggest that a small amount of iron(III) chloride had also been carried up into the film during the deposition process. X-Ray patterns of the pristine multilayers [see Fig.



Scheme 1 The solid state reactions of iron(III) stearate multilayers with hydrogen chloride gas and pyrrole vapour to form conductive polypyrrole. Connected black dots symbolize polypyrrole.

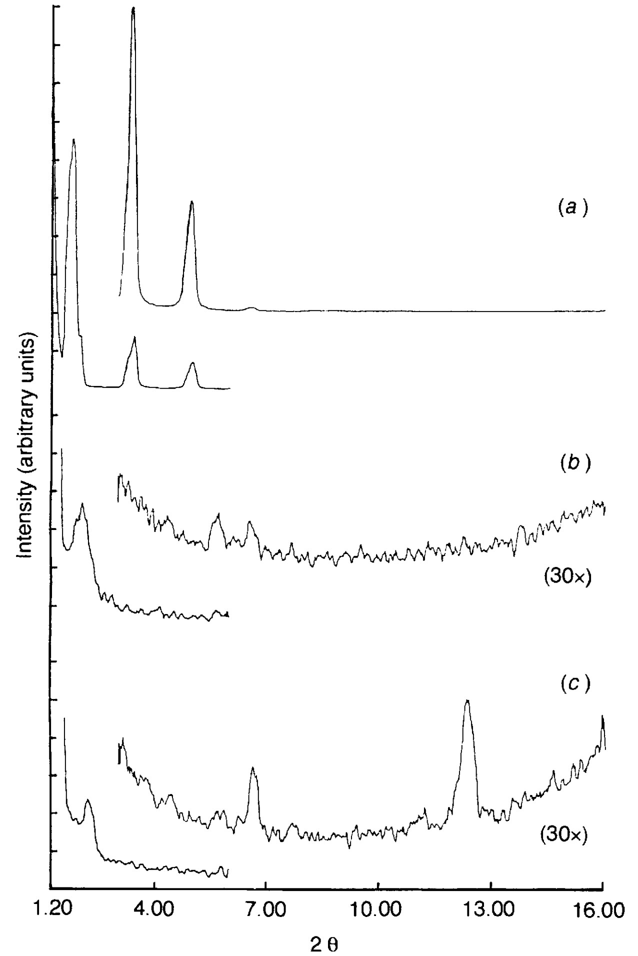


Fig. 1 Small angle X-ray scattering curves recorded from 1.2 to 6° and from 3 to 16° for a iron(III) stearate multilayer (*a*) in pristine form, (*b*) after acid treatment, (*c*) after exposure to pyrrole vapour. Multiplication factors below each curve indicate intensity scale relative to curve (*a*).

1(*a*)] give evidence for a layer structure typical of Y-type LB films of stearic acid salts in which the molecules are aligned in a head-to-head fashion. Calculations of the Bragg diffraction peaks yield a bilayer thickness of about 52 Å.

After sufficient drying, the completed multilayers were suspended in a desiccator which had been charged with hydrochloric acid solution (5 ml, 37%). Upon brief exposure to the HCl gas evolving from the acid (2–7 min), the films became somewhat foggy and attained a slightly grainy texture though the yellow colour persisted. FTIR spectra of the acid-treated films exhibit a strong absorption at 1704 cm^{-1} due to the free acid as well as a diminution of the acid salt peak. Enhanced absorptions at 1584 and 3400 cm^{-1} confirm the presence of iron(III) chloride within the film proving that the first solid state reaction has occurred. The decrease in intensity of the X-ray pattern at this point [see Fig. 1(*b*)] can also be explained in terms of the solid state reaction. The Fe^{III} ions, now in the form of iron(III) chloride, are no longer rigidly anchored to the carboxylate head groups and become scattered within the planes of the multilayer or form separate domains. As a result, they do not play as great a role in the diffraction process so that the consequent X-ray pattern resembles that of a multilayer of pure stearic acid.

The second, and final step in the process is the exposure of the acid-treated film to pyrrole vapour. The LB films were suspended in a desiccator containing pyrrole (5 ml) and evacuated to pressures of 0.3 to 4 Torr in order to saturate the chamber atmosphere with the vapour of the monomer. The system was sealed in this condition and left to stand under a static vacuum for 18 h to insure that the reaction had run to completion. Under these conditions, the pyrrole molecules diffuse into the multilayers (most likely through defect and imperfections in the multilayer), and react with the iron(III) chloride presumably by the same mechanism as the bulk polymerization process. Infrared spectra of the resulting grey films show absorptions in the low frequency regime (1600–800 cm^{-1}) which are identical to the ring vibrations of electrically conducting polypyrrole. In-plane conductivities, as measured by the Van der Pauw method,[12] typically fall within the range of 0.1 to 2 S cm^{-1} although values as high as 10 S cm^{-1} have been obtained. The films also show enhanced stability in ambient conditions relative to films made by direct polymerization on the LB trough. The in-plane conductivity of films left standing in air at room temperature were monitored for 30 days. In this time, the conductivity of films made by this new method decayed to 20% of their initial value while directly polymerized films decayed to 2%.

Perhaps the most intriguing aspect of films made by this new method, aside from their high conductivities, is the emergence of a new molecular structure as evinced by the X-ray spectra of the treated multilayers [see Fig. 1(*c*)]. The nature of this new structure has yet to be determined from the information available, however, it appears that a new type of molecular order has emerged during the polymerization reaction.

The manipulation of LB films *via* solid state reactions has long shown promise in fabricating ultra thin electro-active materials. This new advance in the field demonstrates that the process can be successfully used to fabricate highly conductive polymer films while still maintaining the high degree of organization associated with the Langmuir–Blodgett technique.

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