

## Interfacial polymerisation of anilinium at Langmuir monolayers

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**Anilinium is strongly adsorbed at monolayers of the phospholipid L- $\alpha$ -dimyristoylphosphatidic acid (DMPA) and hexadecanesulfonic acid (HDSA) at the air–water interface, and undergoes chemical polymerisation under conditions where bulk polymerisation does not occur.**

Designing interfaces that promote or direct chemical reactions is of major importance. Well-organised, and tuneable, interfaces are particularly beneficial in this respect and, consequently, the investigation of molecular monolayers at the air–water interface has received much attention.<sup>1,2</sup> Assembling amphiphiles at water surfaces in a Langmuir trough allows exquisite control over the surface pressure and organisation of the molecular interface. In addition, Langmuir films offer the possibility of varying the surface concentration of reactants and reactive sites by controlling the surface pressure. While the properties of such films have been intensively studied and several classes of reactions have been examined,<sup>1</sup> there have been relatively few reports on polymerisation in this environment.<sup>3,4</sup> Moreover, in all studies that we are aware of the monomer was covalently attached to the amphiphile, affecting its mobility and limiting the polymerisation to a monolayer.

Monolayers of conducting polymers are attracting much interest as platforms for nanotechnology and molecular electronics. Consequently, several methods have been reported for the formation of two-dimensional conducting polymer films on solid electrodes.<sup>5–8</sup> Here, we demonstrate the possibility of forming polyaniline, promoted by a Langmuir monolayer, under conditions where bulk polymerisation does not occur. The Langmuir monolayer serves two purposes: (i) to greatly increase the local concentration of the monomer and (ii) to provide a scaffold for the polymer formed.

An anionic phospholipid was selected to ensure that the positively charged anilinium cation would be attracted to the interface. This electrostatic approach, which has been used to assemble mixed monolayers on solid supports,<sup>9,10</sup> contrasts with the covalent attachment of a monomer to an amphiphile, which requires elaborative synthesis and may restrict the reorganisation of the monomer in the course of polymerisation. Fig. 1 shows the clear effect of a small concentration (0.01 mM) of anilinium monomer, introduced into the water subphase, on the pressure–area isotherm for DMPA. The phospholipid (50  $\mu$ L of 0.96 mg mL<sup>-1</sup>) was spread from an 80% CHCl<sub>3</sub>–20% MeOH solution and compressed after 10 min at a speed of 25 cm<sup>2</sup> min<sup>-1</sup> on a Nima (Coventry, UK) trough (max. area 512 cm<sup>2</sup>). The evident change in the isotherm is due to the electrostatic interaction between the anilinium and the anionic phospholipid, which increases the surface pressure at a given area per molecule.

To confirm the presence of anilinium at the interface, we transferred the monolayer (at 10 mN m<sup>-1</sup>, upward deposition, 5 mm min<sup>-1</sup>) to an indium tin oxide (ITO) electrode as a Langmuir–Blodgett (LB) film. To prevent any desorption of the anilinium, the modified electrode was immersed into an electrolyte solution of 0.1 M HCl under potential control (1 V vs. Ag/AgCl) to instantly polymerise the bound anilinium. Fig. 2 shows a typical cyclic voltammogram (CV) of the polyaniline formed in this way. The CV shows the doping/undoping characteristics of a monolayer PAN

film in acidic media, on the anodic and cathodic sweeps.<sup>11</sup> The surface coverage estimated by integrating the charge is less than a monolayer, which is due to a transfer ratio smaller than one in forming the LB film.

Anilinium can be polymerised oxidatively, either electrochemically or chemically.<sup>12</sup> We investigated the chemical polymerisation of the anilinium Langmuir film as a result of adding an oxidant to the subphase. Among the different oxidants that were tested (Ce(vi), S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, Fe(III), Ir(IV), H<sub>2</sub>O<sub>2</sub>), S<sub>2</sub>O<sub>8</sub><sup>2-</sup> was most effective in promoting interfacial polymerisation. Conditions were carefully chosen, by numerous control experiments, to ensure that polymerisation did not occur in the bulk solution on the time scale of the interfacial reaction. We found that it was important to control

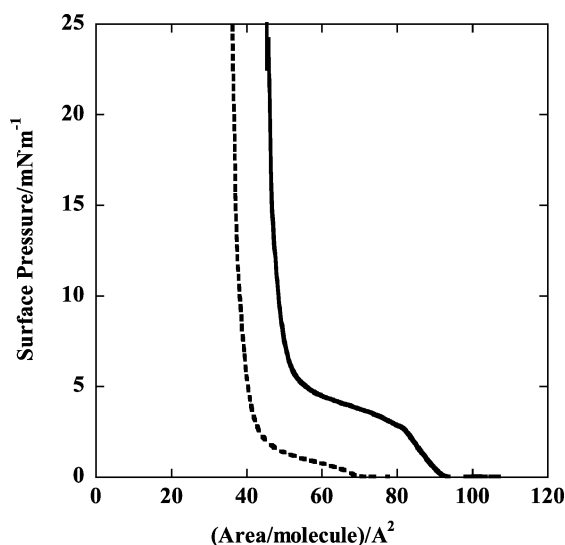


Fig. 1 Pressure–area isotherms of DMPA on water (dashed line) and with 0.01 mM anilinium chloride in the subphase (solid line).

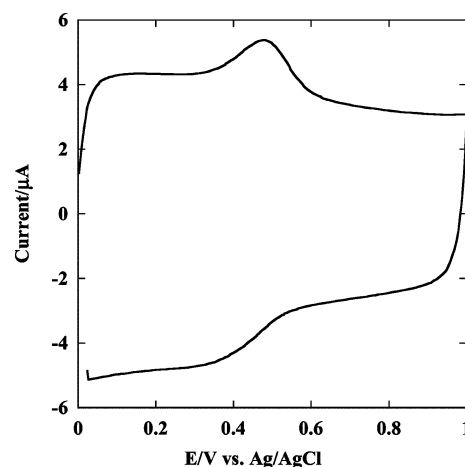
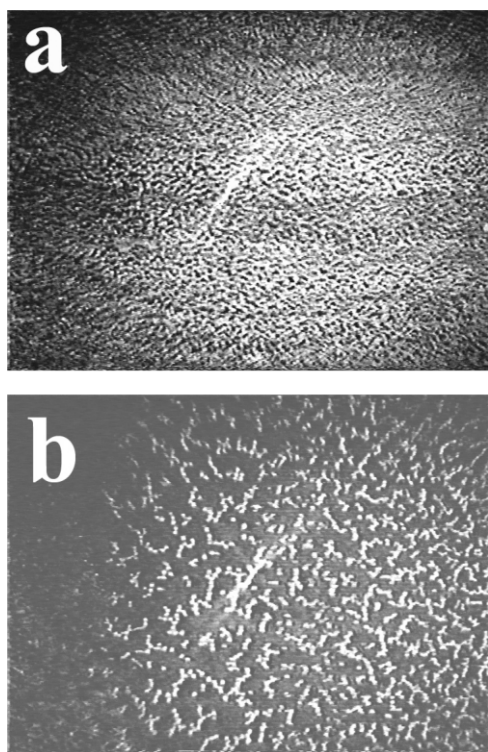


Fig. 2 Cyclic voltammogram (scan speed 0.2 V s<sup>-1</sup>) of a DMPA–polyaniline LB film transferred to ITO in 0.1 M HCl.

the concentrations of the acid (needed to promote polymerisation,<sup>13</sup> as well as to protonate the aniline), anilinium and the oxidant. Experiments carried out in bulk solution, using spectrophotometric detection showed that in the presence of 0.25 mM H<sub>2</sub>SO<sub>4</sub> and 1 mM each of the anilinium and the oxidant, bulk polymerisation was not observed after more than two hours. Increasing the concentration of each species by an order of magnitude resulted in the formation of a blue colour (absorption maxima at 323 and 572 nm) within 30 min, indicative of the onset of polymerisation. Polyaniline, in its emeraldine state, shows these two absorption features,<sup>14</sup> which strongly depend on the protonation state of the polymer.

Following these background studies in bulk solution, polymerisation at the air–water interface was carried out under a variety of conditions, below the threshold identified above. To follow the interfacial reaction we monitored the change of surface area under a constant surface pressure, as a function of time<sup>3,4</sup> with simultaneous Brewster Angle Microscopy (BAM) measurements. We observed negligible change in the molecular area at a range of constant surface pressures (0.5–20 mN m<sup>-1</sup>). However, clear evidence for the formation of polymer at the interface was provided by BAM, with typical data shown in Fig. 3. After establishing the monolayer at a surface pressure of 10 mN m<sup>-1</sup>, with 3 mM H<sub>2</sub>SO<sub>4</sub> and 1 mM each of aniline and persulfate, a uniform polymer layer was formed after *ca.* 20 min, observed as an increasingly bright contrastless image. The formation of a polymer was most evident when the barriers of the Langmuir trough were opened slowly (25 cm<sup>2</sup> min<sup>-1</sup>) to expand the film (Fig. 3a and b). The collapse of the film was clearly accompanied by segregation into filaments of



**Fig. 3** Brewster angle microscope images of polyaniline formed at the water–air interface upon opening the barriers of the Langmuir trough at 25 cm<sup>2</sup> min<sup>-1</sup> from a surface pressure of 10 mN m<sup>-1</sup>: a) after 105 s; b) after 255 s.

material. In the absence of oxidant in the subphase, no such effects were evident.

While there was no area change in this system during polymerisation, it was clearly seen when DMPA was replaced by HDSA. In this latter case, there was an increase of the area per molecule, after an induction time of a few min. However, this system was complicated by the slow and continuous dissolution of the HDSA amphiphile into the subphase (causing a background decrease of the area per molecule), making it difficult to quantitatively analyse the time course of the change in area per molecule. We believe that the striking difference in the characteristics of the HDSA and DMPA systems is attributable to the much smaller cross-sectional area of the single-chained HDSA (*ca.* half that of DMPA) at the water–air interface, making it much more sensitive to the formation of polymer.

In conclusion, we have clearly shown that the interfacial polymerisation of anilinium can be promoted under conditions where the bulk reaction does not proceed at a significant rate. This is most likely because electrostatic attraction of anilinium to the negatively charged amphiphiles leads to very high surface monomer concentrations, that are crucial for the fast polymerisation of aniline.<sup>15</sup> The use of a monolayer template to trap the reactants and increase their local concentration is clearly an approach which could have general applicability, particularly if a selectivity dimension could be introduced into the interfacial process. Finally, our generic approach in which a polymerisable monomer is electrostatically attracted by the Langmuir film is not limited to the formation of a monolayer unlike previous approaches based on covalently bound monomers.

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