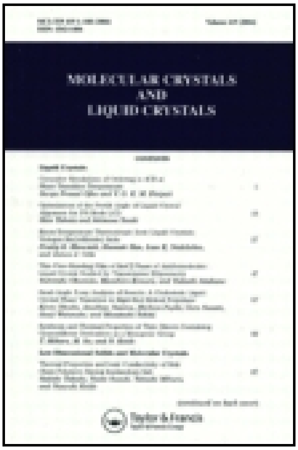

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Some Aspects of Multi-Layer Build-Up of Langmuir-Blodgett Films

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Some Aspects of Multi-Layer Build-Up of Langmuir-Blodgett Films

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The mechanism of multi-layer build up of Langmuir-Blodgett films has been studied using the liquid crystal imaging technique. Two materials were studied ω-tricosenoic acid and cadmium arachidate. Differences in the morphologies of different numbers of layers is discussed and results on the behaviour of defects throughout the film thickness are presented.

1. INTRODUCTION

The mechanism of multi-layer build-up of Langmuir-Blodgett films is an area of relevance to device applications (e.g. optical devices) where the perpetuation and/or growth of defects from the first monolayer may be an important factor in the ultimate performance of the device. Although it is recognised that the substrate and subphase cleanliness are influencing factors in the final film quality little is known or understood about defect generation and control and little information exists as to whether defects perpetuate and increase in both size and number with increasing film thickness or whether they remain contained within a few layers of thickness.

In addition to defects it has been shown that some Langmuir-Blodgett films are composed of crystalline regions (or domains)[1–4,6]

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and recently it has been demonstrated that this crystalline character is present in single monolayers of ω-tricosenoic acid.[5] The fundamental question of whether the morphology of the initial monolayer is continued in the subsequent layers has not yet been conclusively answered. Peterson et al.,[6,7] however, have reported that the use of specific dipping parameters (i.e. a fast dipping speed) for ω-tricosenoic acid results in epitaxial deposition where the original crystallinity and topology of the first monolayer is preserved throughout the thickness of the film. Recently Veal, Peterson and Girling[8] have recorded the achievement of epitaxial deposition of n-alkanoic acids and have used the method to deposit films of a sufficient thickness to allow examination of the physical structure of the film by polarised light microscopy.

In this paper results are presented on work carried out where changes in the morphology of the film with multi-layer build-up were studied using the liquid crystal imaging technique.[9] This technique allows the examination of Langmuir-Blodgett films of any thickness and yields information on film continuity, quality and uniformity and highlights any crystalline nature or defects which may be present. Two materials were studied, ω-tricosenoic acid (deposited onto aluminium and ITO coated glass substrates), and cadmium arachidate (deposited onto ITO coated glass). Photographs illustrating the evolution of the morphology of the first seven layers of ω-tricosenoic acid are shown and evidence is presented which indicates that the morphologies of the first 1–10 layers were very dissimilar, with this dissimilarity decreasing beyond 7 layers. Similar data is included on cadmium arachidate and observations of films consisting of 1 to 17 layers are recorded. Comments are made on the influence of the first few layers on the final bulk film quality and the behaviour of defects throughout the thickness of the film.

2. EXPERIMENTAL DETAILS

2.1. Substrate preparation

The Indium Tin Oxide (ITO) coated glass was supplied by EEV of Chelmsford, Essex. After cutting to size (30 mm × 10 mm) the substrates were subjected to a rigorous cleaning procedure. This involved scrubbing with detergent ("Decon 75") to remove adherent particles and bulk contamination, ultrasonic cleaning in "Decon 75," rinsing in ultrapure water then further ultrasonic cleaning in solvents and drying in a stream of filtered nitrogen. The cleaning procedure used on the substrates for the deposition of ω-tricosenoic acid had minor differences to the procedure used on the substrates for cadmium arachidate. This was not thought to be important as previous studies had indicated that minor changes in the procedure were not found to cause significant differences in the film quality.

Aluminium substrates were prepared by evaporating aluminium on to both surfaces of clean Corning 7059 glass. The metal thickness was approximately 300 microns and the evaporation was performed under a vacuum of approximately 10^{-6} Torr. Immediately prior to film deposition the aluminium substrates were exposed to a low pressure rf discharge then rinsed in pure filtered water and blown dry in nitrogen.

2.2. Film preparation—ω-tricosenoic

All of the ω-tricosenoic acid films were deposited in a commercial trough of the constant perimeter type constructed from soda-lime glass with PTFE rollers and PTFE coated tape forming the barrier. The trough was kept in a clean environment to reduce contamination by dust. The subphase was deionized water with an original resistivity of 18 MΩ cm^{-1}. The water was dispensed through a 0.22 micron filter to remove dust and the deionisation system contained an activated carbon cartridge to remove organic contaminants. Solutions of ω-tricosenoic acid were accurately made up to concentration of 0.2 mgm l^{-1} in 'Aristar' grade chloroform. These were dispensed onto the trough from an all-glass syringe through a 0.2 micron PTFE filter. A fresh filter was used each time and the syringe plus filter were rinsed in chloroform before uptake of the ω-tricosenoic acid solution. After a 1 minute time lapse to allow for solvent evaporation the monolayers were compressed slowly (0.2 Å^2 molecule^{-1} sec^{-1}) to a pressure of 30 dynes cm^{-1}. A period of approximately 10 minutes was normally allowed for the compressed monolayer to stabilise after which film deposition was started. The substrates were immersed in the subphase before spreading of the monolayer and the first layer was transferred on the upward movement of the substrate. This was carried out at a speed of ~ 3 mm min^{-1}. Only films which emerged from the subphase completely dry were used, any that had drops of water on them were discarded. Subsequent layers were deposited at ~6 mm min^{-1}. By varying the depth of immersion it was possible to produce films of different thicknesses on the same substrate. By use of an appropriate sample holder up to six substrates were used simultaneously for film deposition from the same subphase. This allowed direct comparison of film quality between films deposited on aluminium and ITO substrates with many possible variables being excluded by dipping from the same subphase.

2.3. Film preparation—cadmium arachidate

The cadmium arachidate films were deposited in a Landau style trough constructed from PTFE. Again the trough was kept in a clean environment to reduce contamination by dust. The subphase was freshly distilled water to reduce the amount of dissolved CO_2 and contained cadmium chloride with $[(Cd^{2+})] = 5 \times 10^{-4}$ M. The pH was maintained at approximately 5.6.

Solutions of arachidic acid were made up to a concentration of 0.1 $mgml^{-1}$ in 'Analar' grade chloroform and were dispensed onto the trough through a freshly cleaned pipette. The monolayers were compressed at a speed of ~0.2 $Å^2$ $molecule^{-1}$ sec^{-1} to a pressure of 30 dynes cm^{-1}. The initial layer was transferred on the upward stroke at a speed of 1 mm min^{-1} and the subsequent layers at 2 mm min^{-1}.

2.4. Experimental technique

Examination of the samples using the liquid crystal was achieved by making the substrate supporting the film one of the plates of a liquid crystal cell as outlined previously.[9,10] The other plate of the cell was a glass slide treated with an aligning agent such as a chrome complex or lecithin to give homeotropic alignment of the liquid crystal at its surface. The liquid crystal material used in all of these studies was the commercially available E7 supplied by BDH Chemicals of Poole, Dorset.

The samples were viewed through crossed polars by use of a Nikon Optiphot polarising microscope. It was possible to view either in transmission or reflection, depending on the substrate. The resulting images were recorded with either a polaroid or 35 mm camera attached directly to the microscope.

3. RESULTS

3.1. ω-tricosenoic acid

Films of ω-tricosenoic acid were deposited onto ITO and aluminium coated glass substrates as described in Section 2.2. Films with aluminium as the substrate tended to be of a poorer quality than those which had been deposited onto ITO. Despite this feature the same general trends were observed for multi-layer build-up on both types of substrate.

As reported previously[5,9] it was again noted that the quality of the first monolayer immediately adjacent to the film-no film boundary was invariably very poor inducing a non-uniform alignment of the liquid crystal. This was found to be true regardless of the nature of the remaining area of the monolayer. The morphologies of the first few layers (~ 7) were observed to be significantly different and it was always possible to see a clear delineation line between the first and third and third and fifth layers. When good deposition was achieved it was found that the initial monolayer induced, on average, a near homeotropic alignment of the liquid crystal, this being uniform over most of the film area. As before, background structure of a crystalline nature was apparent in all of the examined monolayers and exhibited the characteristic 'flow pattern.' Small defects, between 1 and 10 microns in size, were always observed to be present although the density of these varied from sample to sample and from area to area.

The alignment induced in the liquid crystal by trilayer LB films was significantly different from that induced by the monolayer. The overall alignment was not as uniform and some areas of $\geqslant 100$ microns in size exhibited a large degree of disorder. In addition to this the trilayer contained, on average, a greater density of small defects. There was little evidence of the original crystalline nature of the monolayer being preserved in the trilayer. The variation in the quality of the trilayer from sample to sample was large this being true even if the original monolayers were of a similar standard. It should be noted that the trilayer was always a better film than that part of the monolayer close to the film-no film boundary.

Layers five and seven were generally found to be an improvement on their companion trilayers although they failed to attain the standard of the first monolayer. The induced alignment again tended towards the homeotropic, uniformity over the film area was greater and there were fewer defects. The morphologies of the fifth and seventh layers were very similar and it was often not possible to detect the boundary between the two. It was occasionally possible to observe a crystalline nature to the fifth and seventh layers.

Figures 1 to 3 show the 1–3, 3–5, 5–7 boundaries of a film of ω-tricosenic acid deposited onto an aluminium substrate. Figure 1 illustrates the difference in the induced alignment between the first and third layers with the monolayer exhibiting a uniform near homeotropic state whilst the trilayer is less uniform, has a greater density

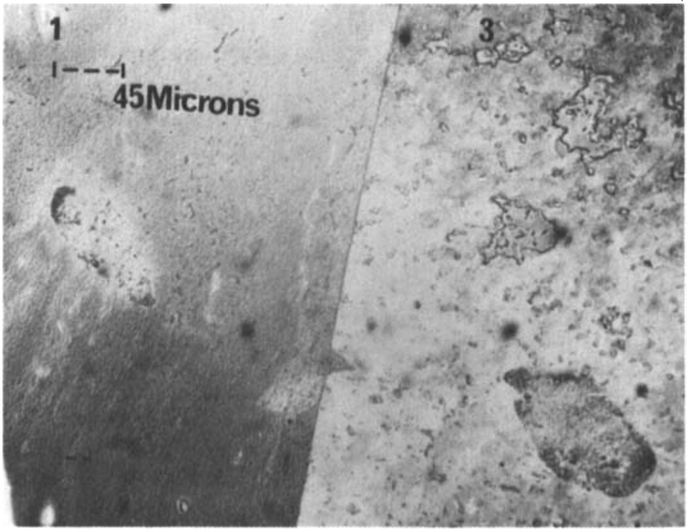

FIGURE 1 1 and 3 layer film of ω-tricosenoic acid on aluminium substrate.

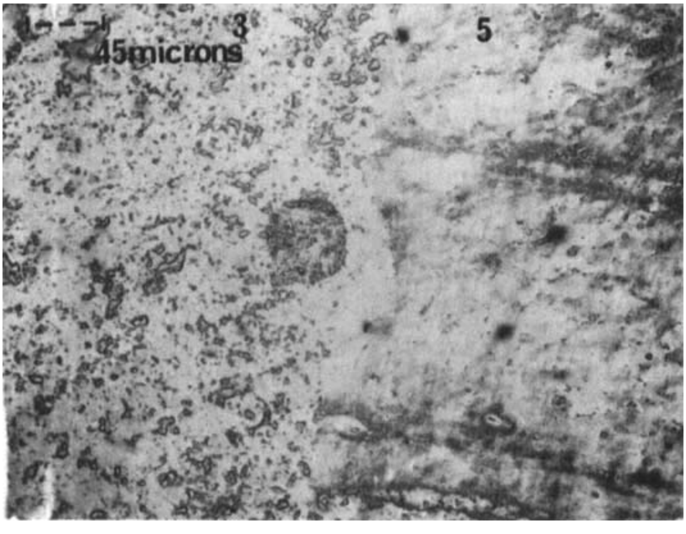

FIGURE 2 3 and 5 layer film of ω-tricosenoic acid on aluminium substrate.

of small defects and some areas of significant disorder. Note the very distinct delineation line between the two thicknesses of film. Figure 2 is a photograph of the third and fifth layers and highlights the increased quality of the fifth layer. Again the delineation line is very

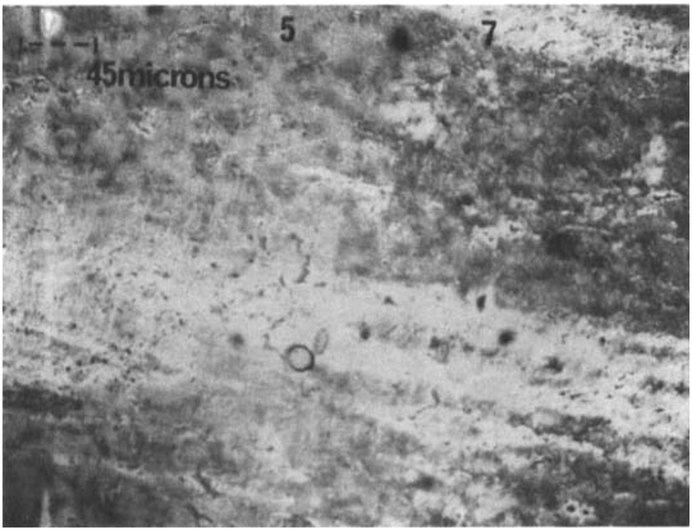

FIGURE 3 5 and 7 layer film of ω-tricosenoic acid on aluminium substrate.

distinct and shows the interesting behaviour of contouring round a defect. Figure 3 illustrates the similarity between the fifth and seventh layers, the boundary between the two being just discernible.

Although the observation was made that a very poor monolayer resulted in a poor multilayer film there were indications that defects did not always perpetuate throughout the film thickness. This phenomenon is apparent in Figure 4 which is a photograph of the 3–5 layer boundary of an ω-tricosenoic acid film on an ITO coated glass substrate. At the centre of the picture is a region of the film which is inducing a large degree of disorder in the liquid crystal, i.e. there is a defect in the film. (The two large black circles also present are bubbles in the liquid crystal cell.) This defect straddles the 3-5 layer boundary and is more pronounced in the third layer than in the fifth. On going from the third to the fifth layer the disorder induced in the liquid crystal by the defect immediately decreases at the boundary indicating that the defect in the LB film itself immediately becomes less pronounced at the 3-5 boundary. This suggests that the deposition of the subsequent two layers resulted in an increased ordering of that part of the film rather than a total perpetuation of the defect throughout the film thickness. This characteristic of defects was often observed both at the 3–5 and 5–7 boundaries but very rarely at the 1–3 boundary.

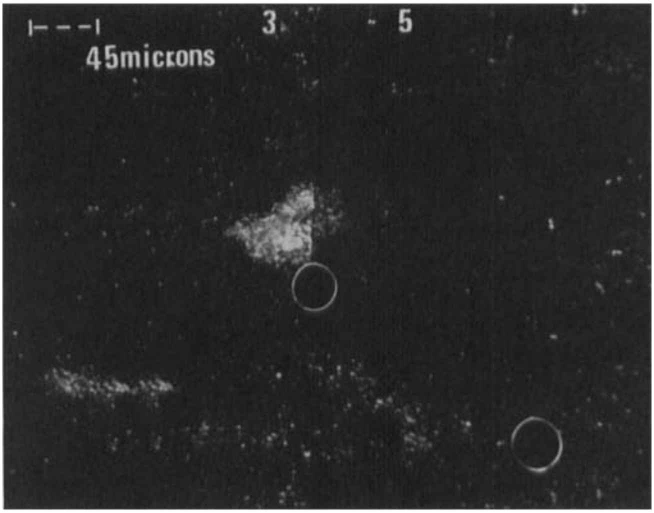

FIGURE 4 3 and 5 layer film of ω-tricosenoic acid film on ITO substrate.

3.2. Cadmium arachidate

All of the cadmium arachidate films in this study were deposited onto ITO coated glass substrates. Films which had been deposited on to aluminium were of such a poor quality that meaningful studies were rendered impossible. The results obtained for cadmium arachidate are very similar to those obtained for ω-tricosenoic acid. As had been found in previous work a single monolayer of cadmium arachidate was observed to induce an alignment in the liquid crystal which was very near homeotropic.[9] In common with ω-tricosenoic acid, trilayers of cadmium arachidate were generally of a poorer quality than the original monolayers, exhibiting many more defects and large regions where the overall alignment was far from homeotropic.

Deposition of subsequent layers did not result in a reproduction of the trilayer characteristics but instead led to a decrease in the density of defects and an overall increase in the uniformity of the Langmuir-Blodgett film, with the alignment again tending towards homeotropic. Figures 5 and 6 illustrate this feature. Figure 5 is a photograph showing the average alignment induced in the liquid crystal by a trilayer cadmium arachidate film and Figure 6 shows the average alignment induced by the companion 17 layer film. The contrast between the two is immediately obvious, with the trilayer ex-

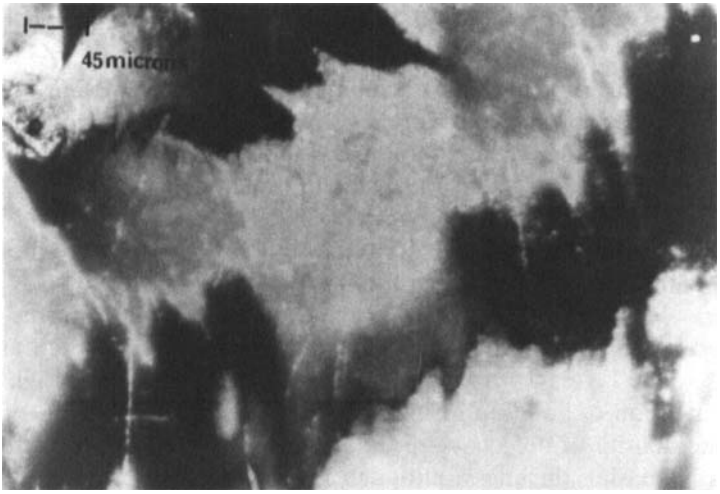

FIGURE 5 Trilayer cadmium arachidate film on ITO substrate.

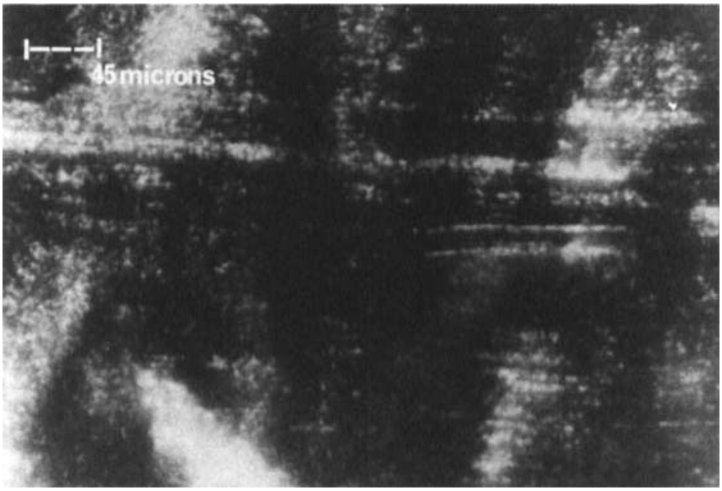

FIGURE 6 17 layers of cadmium arachidate on ITO substrate.

hibiting a large degree of non-uniformity and regions where the alignment is far from homeotropic and the 17 layer inducing an alignment which is near homeotropic and which is much more uniform over the sample area.

4. DISCUSSION

The mechanism of multi-layer build-up of Langmuir-Blodgett films has been studied in two different materials, ω-tricosenoic acid and cadmium arachidate using the liquid crystal imaging technique. The same general trends were found for both materials. With the deposition conditions described, it was found that within the first 1–7 layers the morphologies of different numbers of layers were dissimilar, with these differences becoming less pronounced beyond ~ 7 layers. When good deposition was achieved the initial monolayer was found to be of a high quality and uniform over the sample area. Subsequent layers were found to be of a poorer quality although the continuation of build-up resulted in increased film quality.

The density of defects were, in general, observed not to increase with increasing thickness, although very occasionally a sample was found where the opposite was true—a result which has been previously observed for cadmium arachidate.[9] These differing observations may be explained by postulating the possibility of a dirty subphase in the cases where the defect density was found to increase with film thickness. In addition to these features, it was noted that gross defects did not always appear to fully perpetuate throughout the sample thickness but that instead the disorder in additional layers had decreased.

It should be noted that throughout this study the deposition parameters for each material were held constant and that the results obtained may apply only to the quoted dipping conditions. It is possible that by changing, e.g. the dipping speed, different behaviour may occur. Work is continuing at RSRE to investigate the influence of deposition parameters.

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