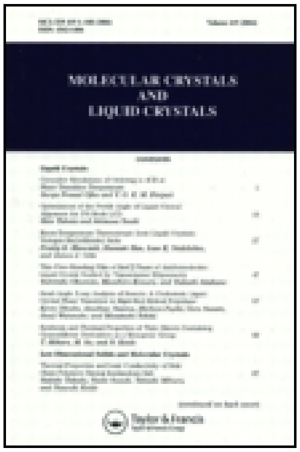

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

A Technique for the Characterisation of Langmuir-Blodgett Films

J. Staromlynska [a], F. C. Saunders [a] & G. W. Smith [a]
[a] Royal Signals and Radar Establishment, St Andrews Road, Gt Malvern, Worcs

Version of record first published: 20 Apr 2011.

To cite this article: J. Staromlynska, F. C. Saunders & G. W. Smith (1984): A Technique for the Characterisation of Langmuir-Blodgett Films, Molecular Crystals and Liquid Crystals, 109:2-4, 233-243

To link to this article: http://dx.doi.org/10.1080/00268948408078709

Mol. Cryst. Liq. Cryst., 1984, Vol. 109, pp. 233–243
0026-8941/84/1094-0233/$18.50/0

A Technique for the Characterisation of Langmuir–Blodgett Films

J. STAROMLYNSKA, F. C. SAUNDERS and G. W. SMITH
Royal Signals and Radar Establishment, St Andrews Road, Gt Malvern, Worcs

(*Received December 2, 1983*)

A method has been developed which allows the characterisation of Langmuir–Blodgett films. The technique utilises the liquid crystal aligning properties of the films and may be applied to films composed of any number of layers. Two materials were studied, ω-tricosenoic acid and cadmium arachidate. Differences between one and three layer samples of these materials are discussed and observed defects down to a size of approximately 1–2 microns are illustrated. Tentative explanations for the occurrence of some of the defects are put forward. The results of a preliminary study of electron beam damage in ω-tricosenoic acid are presented.

1. INTRODUCTION

Characterisation of Langmuir–Blodgett films tends to rely on such methods as electrical measurements[1] and electron and x-ray diffraction.[2–5] Consequently information on film quality (e.g. continuity) and the influencing factors is very limited thus enhancing difficulties in identifying the optimum conditions for good quality film formation. Knowledge of film defects, reasons for their occurrence and their control, is of great importance in many areas. For example the behaviour of defects as a function of film thickness is of particular relevance in the assessment of the suitability of multi-layer films for optical applications and the study of induced damage from lasers is of interest in the context of device performance and reliability.

In this paper we describe a simple method for examining sample quality which utilises the liquid crystal aligning property of the film and which highlights defects down to a size of approximately one or two microns. Results are presented on two different materials, cadmium arachidate and ω-tricosenoic acid. Photographs of different intrinsic defects are shown and a preliminary attempt is made at explaining the origin of some of them. Differences between 1 and 3 layer samples are noted. An initial study was also made of damage in 3-layer ω-acid deliberately induced by exposure of the film to an electron beam. This had the dual purpose of serving as a check on the resolution of the technique and giving information on the problems encountered when using ω-acid as a resist in electron beam lithography.

2. EXPERIMENTAL DETAILS

2.1. Film preparation

All of the LB films were deposited in a commercial trough of the constant perimeter type which was kept in a clean environment to reduce contamination by dust. For monolayers of ω-tricosenoic acid the sub-phase was deionized water with an original resistivity of 18 MΩ cm^{-1}. The water was dispensed through 0.22 μm filter to remove dust. The deionization system contained an activated carbon cartridge to remove organic contaminants. For cadmium arachidate mono-layers the sub-phase contained cadmium chloride with $[Cd^{2+}] = 2.5 \times 10^{-4}$ M. The pH was maintained at ~ 5.8 by the addition of HCl or NaOH.

The substrates for film deposition were commercially available ITO coated glass. After cutting to size they 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 ultrasonic cleaning in chloroform and drying in a stream of filtered nitrogen. As a final cleaning step, immediately prior to film deposition, the substrates were exposed to a low pressure rf discharge then rinsed in pure filtered water and blown dry in nitrogen.

Solutions of arachidic acid and ω-triconsenoic acid were accurately made up to a concentration of 0.2 mg ml^{-1} in 'Aristar' grade chloroform. These were dispensed onto the trough from an all glass syringe through a 0.2 μm PTFE filter. The monolayers were compressed slowly (0.2 $Å^2$ $molecule^{-1}$ sec^{-1}) after a 1 minute time lapse to allow for solvent evaporation. The substrates were normally immersed in the sub-phase before the monolayers were spread and the first layer was transferred on the first upward movement of the substrate. This was carried out at a speed of approximately 3 mm min^{-1}. Only films which emerged from the sub-phase completely dry were used, any that had drops of water on them were normally discarded. Subsequent layers were deposited at a speed of ~ 6 mm min^{-1}. All of the film deposition took place within one hour of the initial spreading of the monolayer.

2.2. Experimental technique

In order to study the alignment induced in a liquid crystal layer by an LB film, the substrate on which the film had been deposited, was used as one of the plates of a liquid crystal cell. The construction of such a cell is both simple and quick although care must be taken in the handling of the glass substrates to avoid damaging or contaminating the film, both of which would affect the subsequent alignment.

The Langmuir–Blodgett sample was placed film side up so that a small quantity of the liquid crystal material could be spread onto the surface. Two strips of a suitable spacing material, such as 12 μm thick 'Mylar', were placed along the edges of the substrate. The top plate of the cell was treated to give homeotropic orientation to the liquid crystal at its surface. This can be achieved by a variety of methods such as treatment with a solution of lecethin (in propan-2-ol at a concentration of 0.01% by weight) or a chrome complex. Similar results were observed using both techniques. The cell was then assembled and clipped together to give a relatively uniform thickness of liquid crystal confined between the two substrates.

The sample was viewed in transmission or reflection by use of a polarising microscope. Initial observations were carried out at low magnification to allow investigation of the overall uniformity of alignment in the liquid crystal layer and hence identification of the extent of the sample film. When viewed through crossed polarisers the sample would be dark and invariant to rotation only if the film was producing a homeotropic orientation in the liquid crystal layer. (Any slight tilt in this orientation could be investigated using conoscopic techniques). In addition any defects in the film would readily be shown as coloured birefringent areas in the uniform dark background.

Observations established that there was always a clear delineation between the substrate without the LB film and the coated substrate. This showed that the homeotropic alignment agent on the top glass substrate was not corrupting the alignment of the liquid crystal on the film.

The liquid crystal material utilised in the majority of these experiments was E7 (available from BDH Chemicals of Poole, Dorset), although similar results were observed with other materials.

3. RESULTS

3.1. Cadmium arachidate

One of the first materials investigated using this method was a one and three layer sample of cadmium arachidate deposited onto ITO coated glass as described in section 2.1. Figure 1 shows the well defined boundary between the monolayer and trilayer regions of the sample where the difference in the induced alignment of the liquid crystal can be seen. The monolayer (at the top of the picture) induced a near homeotropic alignment in the liquid crystal. Subsequent conoscopic examination suggested the occurrence of a small tilt from the vertical along the direction of pull from the trough. The three layer region induced a much greater tilt angle in the orientation of the LC

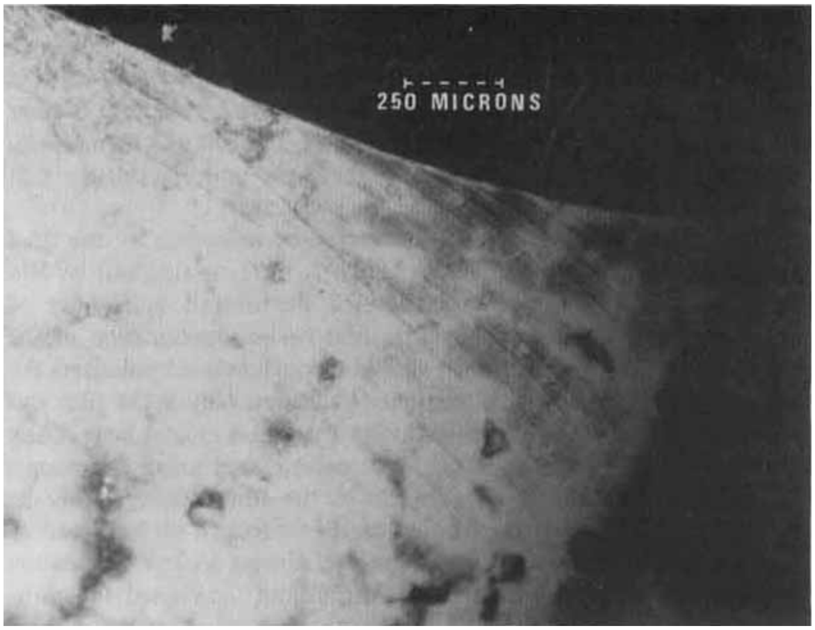

FIGURE 1 1 and 3 layer film of cadmium arachidate, with the 3 layer region exhibiting striations.

layer. In addition a fine structure of dark lines can be seen running perpendicular to the dipping direction at a repeat spacing of approximately 100 μm. Looking at the edge of the substrate these dark lines appear to bend in the opposite direction to the trilayer meniscus. We suggest that these striations are a feature associated with "meniscus jumping" which was observed to occur during the dipping of the second layer resulting in a non-continuous alignment of the molecules in the LB film. Thus the pattern of orientation induced in the liquid crystal by the third layer is indicating the occurrence of defects in the second layer which would presumably build up with each subsequent layer. The dark lines indicate those regions of the film which aligned the LC homeotropically whereas the regions between aligned the liquid crystal at some tilt angle, (which may not be uniform across the stripe), to the drawing direction. Other samples of this material, deposited under similar conditions, all tended to show this pattern of striations. Building up samples to seven layers revealed an increasing disorder in the LC orientation with the striations being more pronounced. This may well indicate a less uniformly aligned surface layer of the LB film.

FIGURE 2 Photograph of a 3 layer cadmium arachidate film, showing a hole in the film.

FIGURE 3 3 layer cadmium arachidate film with deliberately induced scratches.

Defects in the form of discontinuities in the film can also be observed using this technique. Figure 2 shows such a hole; note that the dark 'meniscus' line is bent around the feature suggesting some contamination of the substrate prior to depositing the film. This contrasts with the deliberately induced scratches shown in Figure 3 where the damage is clearly seen to cut across these dark lines.

3.2. ω-tricosenoic acid

The aligning behaviour of LC samples on thin films of ω-tricosenoic acid was observed to be subtly different to that seen on cadmium arachidate. Figure 4 shows that the monolayer region does not give a uniform alignment of the liquid crystal whilst the trilayer region induced a near perfect homeotropic orientation. It was possible to induce similar types of striations to those observed in cadmium arachidate. These striations tended to appear when the films were seen to come out of the trough wet rather than dry. Changing the preparation of the substrate removed these features.

Some small crystalline defects of approximately 1 μm in size were observed in the near perfect trilayer films. Other workers[6] have

FIGURE 4 Photograph of 0, 1 and 3 layers of ω-tricosenoic acid showing difference in alignment of the 1 and 3 layer regions.

reported the appearance of small scale domain features in thicker layers of this and other materials. It would thus be of interest to study more fully the development of these 'crystallites' and examine their build up with increasing layer thickness.

3.3. Induced damage

It is now widely accepted that some Langmuir–Blodgett films are very sensitive to electron beams. This property is a disadvantage when electron beam diffraction is used as a method of characterising the structure of films. It has however been turned to advantage in the area of electron beam lithography where various materials in LB film form are being assessed as possible resists. ω-tricosenoic acid[7,8] has been studied in this context with attention being focussed upon obtainable line widths and the effect of the charge density induced by the electron beam. To date most work has been carried out on multi-layer (20 or more) films with subsequent electron microscopy allowing inspection of the results of exposure. In this work some initial experiments were performed with the aim of making a preliminary study of the effect of electron irradiation on films with only a few layers.

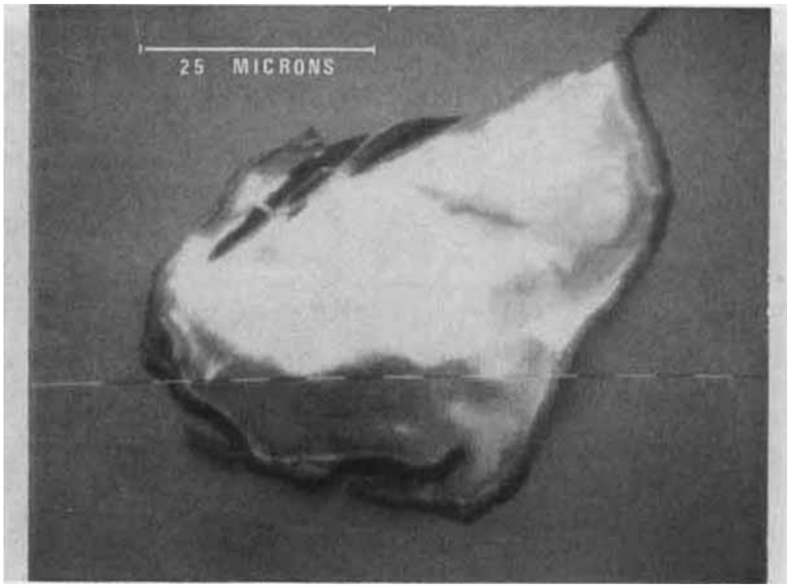

FIGURE 5 Electron micrograph of foreign body on the surface of a 3 layer ω-acid film.

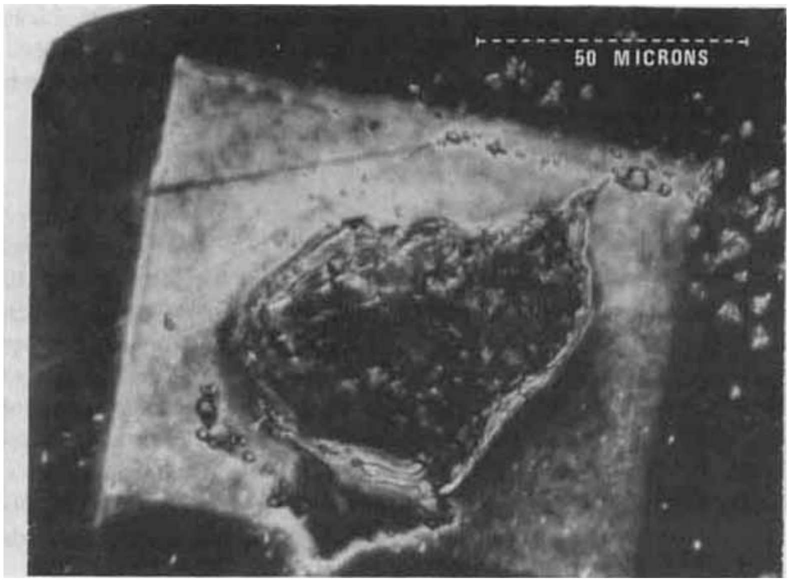

FIGURE 6 Image as seen through polarising microscope of foreign body plus e beam damage after application of liquid crystal.

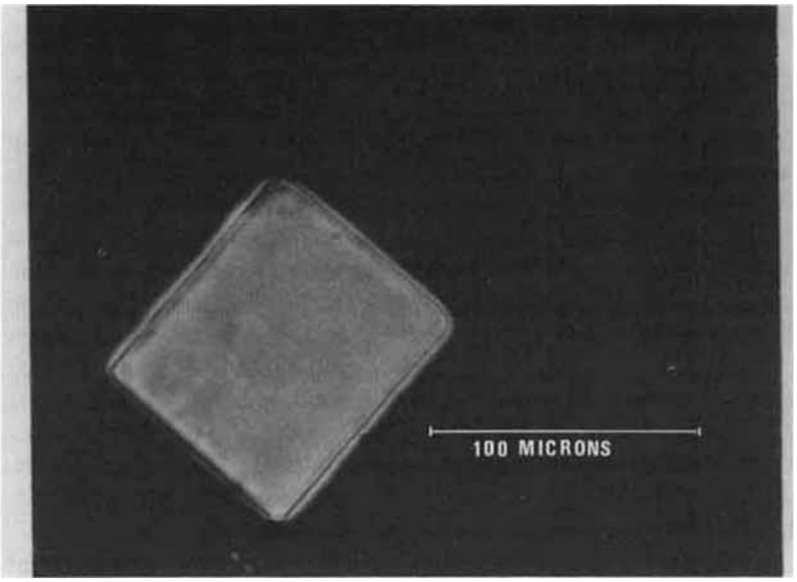

FIGURE 7 Effect of e beam irradiation (100 $\mu C/cm^2$) on good quality 3-layer ω-acid film.

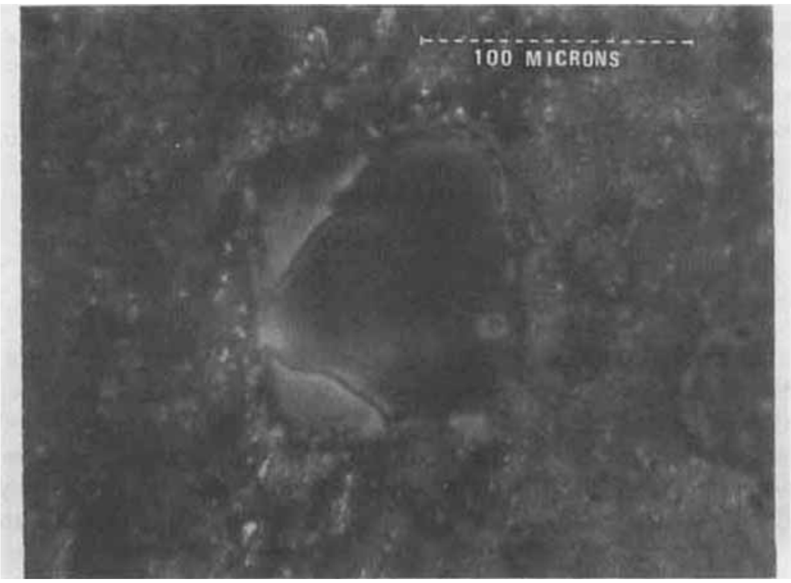

FIGURE 8 Effect of e beam irradiation (100 $\mu C/cm^2$) on poor quality 3-layer ω-acid film.

Three-layer ω-acid films were prepared on an ITO/Glass substrate as described in section 2.1. Irradiation was carried out using a Philips PSEM 500 scanning electron microscope under a vacuum of $\sim 10^{-6}$ Torr. No attempt was made to control the sample temperature during exposure to the beam. The spot size of the beam was 320 Å in all cases and the accelerating voltage was either 25 kV or 6 kV. Figures (5) and (6) highlight the effect of the electron beam: in this case the accelerating voltage was 25 kV, the microscope was in TV scan mode and the exposure time was approximately 10 minutes. No charging up of the film was observed during exposure. Figure 5 is an electron micrograph of a foreign body lying on the surface of the film and Figure 6 is the image as viewed through an optical microscope with crossed polars after application of the liquid crystal. The scan area appears white as it reoriented the liquid crystal away from normal to the surface. We do not believe that the exposed area developed any holes but rather that the material changed character e.g. polymerised.

Further experiments showed that an exposure of $\sim 100\ \mu C/cm^2$ produced a similar, though not identical, effect. The results of irradiation were found not to be totally reproducible from film to film, but were instead dependent upon film quality. Good films exhibited scan areas which produced a uniform alignment (Figure 7) whereas poor quality films tended to induce variable alignment over the exposed surface and in some cases exhibited holes (Figure 8). No obvious difference was observed between irradiation at 25 kV and 6 kV. It is thought that any additional spreading at 25 kV due to backscatter from the substrate was too small to be resolved by the technique. Increasing the charge density to $> 500\ \mu C/cm^2$ resulted in spreading and ill defined scan areas. It was possible to introduce well defined squares of $\simeq 5 \times 5\ \mu^2$ at a charge density of $100\ \mu C/cm^2$.

4. DISCUSSION

It has been shown that the structure of the first few monolayers have a direct bearing on the final quality of a Langmuir–Blodgett film. Attempts at examining the surface structure of LB films have been made in the past, ranging from direct optical microscopy,[6,9] to the Nomarski technique,[10] to evaporation of thin films of metal, (eg silver), with the aim of reproducing the surface texture.[11] In all but one case, many layers have been needed to facilitate such examinations and hence information on the first few layers and their importance has been indirect. We have developed a method which allows inspection of the physical characteristics of any number of layers providing the film has liquid crystal aligning properties. Resolution of the method is determined by the optics used and we estimate that with a good microscope defects of the order of 1 micron may be seen. No limitation is placed on the film substrate as the image may be viewed in both a transmission and reflection mode.

We believe that one of the main areas of application of this method will be in the identification and control of defects, with particular relevance being in the technology of producing high quality multi-layer structures where a good understanding of the role of the first few layers is necessary. It also offers a quick simple mechanism for studying damage induced by external factors (lasers, electron beams) and the dependence of this damage on parameters such as substrate material and thickness, film thickness etc. Work is continuing at RSRE on both the above topics. Further work will also include an investigation of the possibility of reproducibly inducing controlled tilt in the layer by irradiation with an electron beam.

Acknowledgments

The authors wish to thank Mrs. D. Dosser for her assistance with the electron beam irradiation and Drs. M. F. Daniel and K. J. Harrison for useful discussions.

References

1. G. G. Roberts, P. S. Vincett, W. A. Barlow, *J. Phys. Chem Solid State Phys.*, **11**, 2077–2085 (1978).
2. J. F. Stephens, C. Tucklee, *J. Appl. Crystallogr.*, **2**, 1 (1969).
3. G. Lieser, B. Ticke, G. Wegner, *Thin Solid Films*, **68**, 77–90 (1980).
4. A. Banerjie, J. B. Lando, *Thin Solid Films*, **68**, 67–75 (1980).
5. M. Sarkar, J. B. Lando, *Thin Solid Films*, **99**, 119–126 (1983).
6. F. Grunfeld, C. W. Pitt, *Thin Solid Films*, **99**, 249–255 (1983).
7. A. Barraud, C. Rosilio, A. Ruaudal-Teixier, *Thin Solid Films*, **68**, 91–98 (1980).
8. A. Barraud, *Thin Solid Films*, **99**, 317–321 (1983).
9. C. W. Pitt, L. M. Walpita, *Thin Solid Films*, **68**, 101–127 (1980).
10. G. Fariss, J. Lando, S. Rickert, *Thin Solid Films*, **99**, 305–315 (1983).
11. S. C. Steele, M. N. Wybourne, D. Mobius, *Thin Solid Films*, **99**, 117–118 (1983).