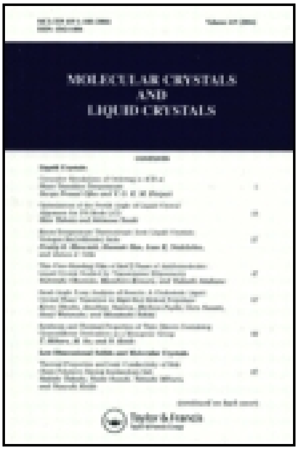

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Ultra-Thin Films of Smectic Liquid Crystals on Solid Substrates

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Ultra-Thin Films of Smectic Liquid Crystals on Solid Substrates

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Molecules which form Langmuir-Blodgett (LB) films are, in many respects, similar to molecules which can form smectic liquid crystals. It is thus surprising that there is such a small overlap in the literature between these two fields of study. In this paper a review of publications dealing with this overlapping region is given. Films analogous to those formed by the LB method can also be formed by thermal evaporation *in vacuo* and by the transfer of freely suspended films of liquid crystals initially formed across apertures in thin glass or metal plates. Some instances of these two techniques are also discussed

Keywords: Langmuir-Blodgett; Smectic Liquid Crystal; Thin Films

INTRODUCTION

The molecules of compounds which form smectic liquid crystals tend to be elongated and to have dipole moments which lie along their axes. The same general description applies to compounds which can form Langmuir-Blodgett (LB) multilayers[1,2,3]. Indeed, this situation might be expected as the structure of a smectic liquid crystal and the structure of an LB film are very similar. It is thus surprising that very few reports exist in the literature of the formation of LB films from compounds known to form smectic crystals. One might also have expected that more workers in the LB field would have attempted to find out if the materials which they had studied would form conventional smectic liquid crystals.

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[*] Corresponding Author.

This article is a review of the very limited literature concerning the overlap between these two fields. One of the interesting aspects of the LB technique is the possibility of forming ultra-thin films consisting of the superposition of a very few monolayers of the compound under study. Very thin films of smectic liquid crystals can also be obtained by freely suspending the films across small apertures and it is possible to deposit such films on solid substrates. Because of the close relationship between the two fields, studies based on this technique are discussed. Some mention will also be made of very thin films formed by thermal evaporation *in vacuo*.

It is important here to point out that there are many papers in the titles of which the expressions 'liquid crystal' and 'Langmuir-Blodgett film' occur which are not relevant to the present discussion and to which no reference will be made. These include studies of the properties of amphiphilic materials at the air/water interface. Here phase changes can occur which are in some ways analogous to the phase changes which take place in true three dimensional liquid crystals. A few papers have been devoted to the formation of LB multilayers of polymers whose side chains show liquid crystalline properties. However, as Ali-Adib *et al* [4] have shown, the structures of such LB films are largely determined by the polymeric nature of the material rather than the behaviour of the side chains and we will thus not refer to this topic.

EXPERIMENTAL METHODS

The deposition of LB multilayers has been described in various books [1,2,3] and reviews articles and will not be further discussed here. However, the characterisation of these films is often far from thorough and the techniques which can be employed deserve mention. It is often assumed that, if the individual monolayers appear to deposit regularly, and if ellipsometry or some other technique shows a regular increase in thickness with the number of layers deposited, then a good regular layer structure has been achieved. However it is often the case that such a film fails to show any regular layer structure when studied by low angle X-ray diffraction. Thus, to be sure that a real LB multilayer has been formed, an X-ray study is essential. If films are deposited on a transparent substrate optical microscopy can be used to study the degree of regularity within the plane of the film. In order to examine in-plane structure on a scale beyond the reach of the optical microscope scanning tunnelling microscopy (STM) and atomic force microscopy (AFM) have both been used successfully. The traditional optical techniques used to characterise films of liquid crystals and discussed, for example, by Gray and Goodby[5] are not really applicable in the case of ultra-thin films and are usually applied to films having a typical thickness of about 10 μm. In the case of LB films we are dealing with from one monolayer (of the order 3 nm) to a few hundred monolayers at the most.

It is helpful to use differential scanning calorimetry (DSC) on small bulk samples of the compounds studied and to compare the temperatures at which phase changes occur with evidence for phase changes in ultra-thin films studied with the aid of a heated stage and a polarising optical microscope.

Langmuir-Blodgett films are usually deposited at or near room temperature the extreme practical limits being 5 °C and 30 °C. We are not aware of the successful deposition of such a film using a smectic compound at a temperature above its crystal to liquid crystal transition.

CYANOBIPHENYL COMPOUNDS

There have been several attempts to form LB films using cyanobiphenyl compounds but none have been successful. Nevertheless these compounds have important technical applications and are widely available and their deposition onto various solid surfaces has thus been extensively studied.

Rather than use the full systematic chemical nomenclature it is more straight forward to use the expressions (nCB) for the alkyl cyanobiphenyls and (nOCB) for the alkoxy cyanobiphenyls where n is the number of carbon atoms in the alkyl or alkoxy chain. See Figure 1.

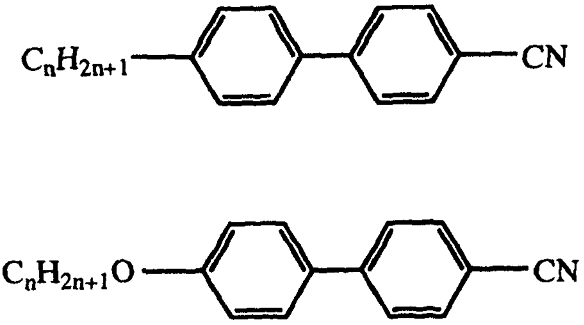


FIGURE 1 Cyanobiphenyl Compounds. (nCN) and (nOCB)

Many studies of the adsorption of these compounds on various surfaces have been made. Some, such as the work of Barmentlo *et al* [6] and Mullin *et al* [7], depend on second harmonic generation and thus on indirect inference. Several direct studies have been made using STM. The difficulty of this technique is that the substrate must possess a degree of electrical conductivity and a highly planar surface. Of particular interest are the results obtained by Iwakabe *et al* [8] using freshly cleaved surfaces of crystals of molybdenum disulphide as substrates. They studied (8CB), **1**, and mixtures of this compound with (12CB), **2**, by depositing small drops of the liquid crystal on the substrate at 100 °C and then cooling to room temperature and the scanning at the liquid crystal/crystal interface using a platinum/iridium tip. Figure 2 is a schematic diagram of how (8CB) deposits which is based on their results. (12CB) deposits in a similar manner. It is interesting that the molecules, though ordered, are prone on the substrate surface though other evidence suggests that multilayers exist with the molecule axes nearly normal to the surface. Results for such compounds using other substrates have been obtained by Mogonov *et al* [9,10].

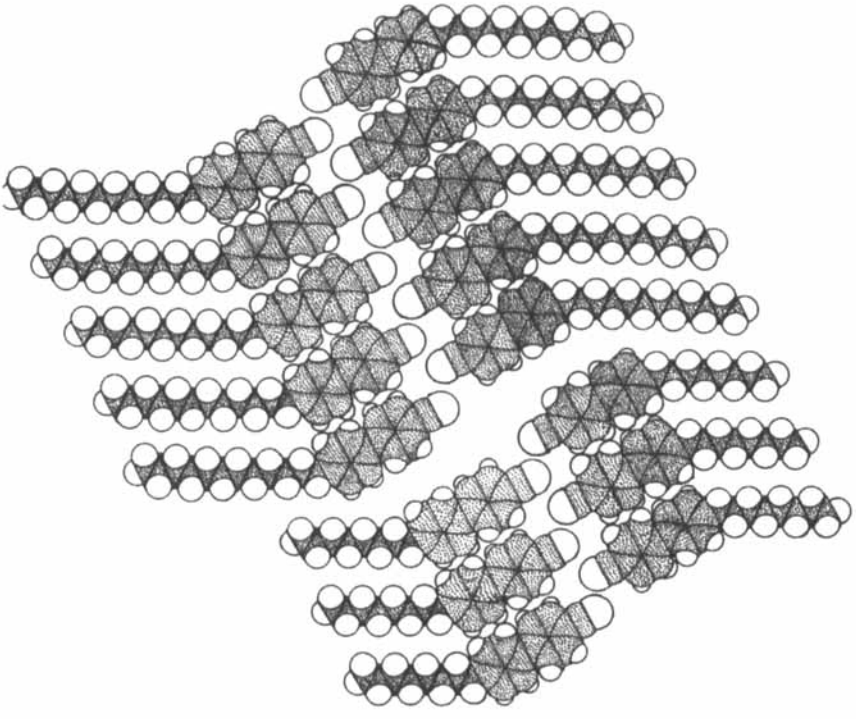


FIGURE 2 How (8CB) deposits on molybdenum disulphide according to Iwakabe *et al* [8]

Itaya *et al* [11] have studied films of (12OCB), **3**, deposited by evaporation *in vacuo* either on quartz plates rendered hydrophilic by cleaning with a chromic acid mixture or hydrophobic by octyltrichlorosilane adsorbed from a hexadecane solution. They used AFM so that there was no need to have a conductive substrate and obtained a film consisting of three dimensional crystallites which did not form a homogenous layer structure. Itaya *et al*[12] deposited (8OCB), **4**, *in vacuo* on o both hydrophilic and hydrophobic substrates and have used fluorescence spectroscopy to characterise their films. Their results support the view that the molecule axes are nearly normal to the substrate surface and that the molecules form an interpenetrating Y structure. (In the language of the LB fraternity a Y structure consists of alternating layers of amphiphilic molecules whose hydrophilic parts are adjacent to one another as are the hydrophobic parts). However photomicrographs obtained by these authors show that, both for hydrophilic and for hydrophobic substrates, the structure of their films are not totally uniform.

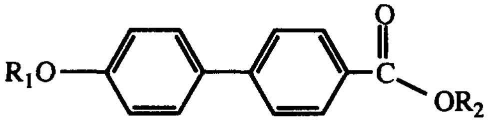
Olbrich *et al* [13] and Ocko [14] studied relatively thin films of cyanobiphenyl compounds which were deposited on various substrates. They used low angle X-ray diffraction and observed a number of Bragg peaks corresponding to the repeat distances which one would expect from the properties of the bulk materials. They concluded that a regular layer structure parallel to the plane of the substrate had been produced in each case. However Woolley *et al* [15] deposited films of (8CB), **1**, and (9CB), **5**, by evaporation *in vacuo*. Their films had a thickness of about 100 nm. They used a variety of substrates and, in every case, observed Bragg peaks at the expected places. When they studied their films by optical microscopy they always found that the film had congealed into a large number of small droplets and had not wetted the substrate. Thus a multilayer structure existed within each droplet and was responsible for the X-ray diffraction. Here one is dealing with a film having a mean thickness of about 100 nm with one surface in contact with the substrate and one surface in contact with air. This is quite different from the way liquid crystal films are normally studied where both sides of the film are in contact with a solid surface and the film has a typical thickness of 10 μm.

The picture that emerges from these results together with many others not cited here is as follows. The layer of a cyanobiphenyl compound immediately in contact with a solid surface resides with the molecules prone on the surface. If the surface has been specially treated the molecules will be oriented in one chosen direction. However, in the case of a thin film having one free surface, the molecules will reside with their long axes roughly normal to the solid surface on which they have been deposited and will congeal into droplets. If the film is formed at a temperature which lies below the crystal to smectic transition temperature and is maintained below this temperature it will probably form many small crystallites. However, as we are only aware of one case in which the latter situation has been studied [11] this generalisation can not be taken for granted. Moreover there are a number of cases of other compounds which can form smectic liquid crystals which form good regular thin films. These compounds are considered in the next section of this paper.

LANGMUIR-BLODGETT FILMS

Most of those compounds which can form both smectic liquid crystals and LB films contain the biphenyl group. Decher and his collaborators [16,17,18] studied a group of n-alkoxy-biphenyl-4-carboxylates whose structure is given in Figure 3 and the attached table. (Compounds **6**, **7**, **8**, **9** and **10**) Compound **7** was of most interest as it had a crystal to smectic phase transition as indicated by DSC well above room temperature (probably about 197 °C) and exhibited 100% deposition in both the upward and downward directions. Moreover these authors studied LB multilayers of this compound by X-ray diffraction and obtained 21 orders of Bragg peaks [16] which indicates a high level of order in the films. Compound **10** could be deposited as LB layers[17] though the resulting order was much lower than that obtained with compound **7**. It underwent a crystal to smectic phase transition at 72° C. These authors also studied this compound in the form of films which were freely suspended initially and subsequently deposited on a solid substrate. This topic will be returned to below.

Woolley *et al* [15] studied a group of compounds, **11**, **12**, **13**, **14** and **15** which are, in some ways, similar to compounds **6**, **7**, **8**, **9** and **10**. Their structures are shown in Figure 4 and the accompanying table. Compounds **12**, **13**, **14** and **15** could be deposited by thermal evaporation *in vacuo* and gave regular layer structures as shown by X-ray diffraction. However only compound **15** showed a *d* spacing which corresponded to two molecular lengths and thus a Y structure. The others showed *d* spacings corresponding to one molecular length and thus, presumably consisted of regular layers in which there was a random arrangement of upward and downward pointing molecules. Compounds **14** and **15** could be deposited by the LB method though only **15** gave a Y structure. The phase changes of this family of compounds were studied by DSC, by the optical methods described by Gray and Goodby [5] and as ordered ultra-thin films using of a polarising microscope and a heated stage. In the latter method those phase changes which produce a disappearance of tilt with increasing temperature can be easily recognised. Though there is some thermal hysteresis, the temperatures at which these phase changes can be detected by the three different methods agree quite well. In all cases thermal equilibrium leads to a crystalline phase existing to well above room temperature.

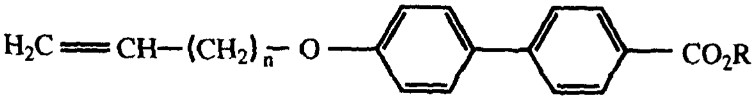


Compound	R_1	R_2
6	$-C_7H_{15}$	-H
7	$-C_7H_{15}$	$-CH_3$
8	$-C_7H_{15}$	$-C_2H_5$
9	$-C_8H_{17}$	$-CH_3$
10	$-C_8H_{17}$	$-C_2H_5$

FIGURE 3 The family of compounds studied by Decher *et al* and described in references [16,17,19]

Bardosova *et al* [19] made a further study of compounds **13** and **15**, namely those which had an isopropyl ester termination, and showed that the structure of multilayers of them formed by evaporation *in vacuo* slowly changes with time. When studied by X-ray diffraction newly formed films of **13** exhibit a mixture of two phases whose *d* spacings are 2.13 nm and 2.21 nm. When such films are stored for a week at room temperature the phase having a *d* spacing of 2.23 nm disappears. It seems probable that the two phases correspond to the well known liquid expanded and liquid condensed phases (See reference 1 pages 50–57) observed in the case of Langmuir-Blodgett films of carboxylic acids and which correspond to films in which the molecular tilt is towards the nearest and next-nearest neighbours respectively. In this case the phase with the smaller repeat distance would correspond to the more tightly packed and more stable phase. Films of compound **15** also show a change of structure with time but here the behaviour is more complex and the reader is referred to the original paper [19] for a further discussion.

Novak *et al* [20] studied the behaviour of an interesting azobenzene derivative, **16**, whose structure is shown in Figure 5 They spread this compound at the air/water interface and formed multilayers by the Langmuir-Schaefer or horizon-



Compound	n	R
11	3	$-C_2H_5$
12	6	$-C_2H_5$
13	6	$-CH(CH_3)_2$
14	9	$-C_2H_5$
15	9	$-CH(CH_3)_2$

FIGURE 4 The family of compounds studied by Woolley *et al* and described in reference [15]

tal lifting method [21]. Here the substrate surface is held nearly horizontal and gently lowered till it is in contact with the water. It is then lifted and the process is repeated. This method of deposition is more difficult to manage than the LB technique but will sometimes allow the deposition of multilayers of compounds which will not deposit in the LB manner. Furthermore, as in this case, it can be used to form structures in which all the molecules point in the same direction and are non-centrosymmetric and hence polar. Below approximately 100 °C multilayers of this compound showed a marked pyroelectric effect which disappears irreversibly above this temperature. X-ray diffraction studies show that newly formed films have a *d* spacing of 3.9 nm but films which have been heated to above 100 °C have a *d* spacing of 6.9 nm and are thus, to a certain extent, in a Y structure. At approximately 114 °C there is a phase change from a crystal to a smectic structure. Two further phase changes occur at 124 °C and at 136 °C and the compound finally melts at approximately 152 °C.

It is of interest to be able to polymerise multilayers of compounds while in the smectic phase and thus stabilise a structure which does not consist of 2D crystallites but does possess a regular layer structure. This is particularly useful in optical applications where the interfaces between the 2D crystallites which tend to occur in many LB films scatter light. With this object in view Bardosova *et al*

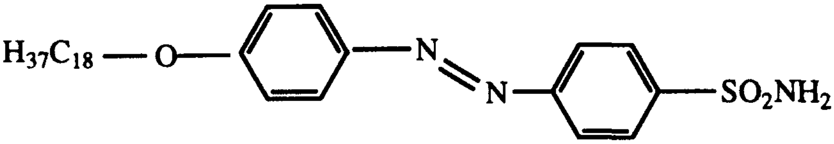


FIGURE 5 The compound studied by Novak *et al* [20]

[22,23] studied the esters of various fumarate compounds. The structure of the most interesting member of this group, **17**, is shown in Figure 6. It could be deposited both by thermal evaporation *in vacuo* and also by the LB method. Multilayers of this compound exhibit a crystal to smectic B phase change at about 56 °C, a temperature which agrees fairly closely with that of a phase change observed by DSC in the bulk material. There is a very large thermal hysteresis associated with this phase change so that multilayers continue to appear isotropic when studied by the polarising microscope for as long as 24 hours after cooling. Furthermore illumination of multilayers of this compound using UV light and a nitrogen atmosphere stabilise this isotropic phase so that it remains indefinitely. Films so treated are only slightly dissolved by heating them in THF for over 70 hours. GPC (gel permeation chromatography) studies of solutions formed in this way indicate that the soluble part consists of a polymer having an average chain length of 84 repeat units. It is to be presumed that the insoluble part either consists of much longer chains or consists of cross linked polymer chains.

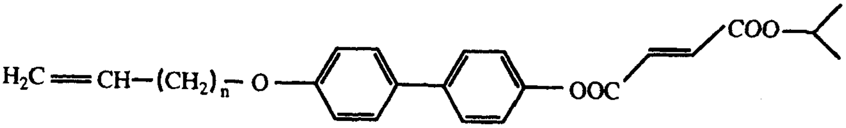


FIGURE 6 The compound, **17**, studied by Bardosova *et al* [22,23,24]

These authors also studied a similar compound differing only in the absence of the double bond in the tail unit, **18**. It is remarkable that this change should remove all the interesting properties which **17** possesses. Thus **18** changes back rapidly to the crystalline phase on cooling through the smectic to crystal phase change and it shows little evidence of polymerising. In principle such a compound could polymerise or cross link both via the fumarate group and also via the double bonds in the tail. To elucidate this matter Bardosova *et al* [24] illuminated monolayers of this compound at the air/water surface using UV light and then deposited multilayers of it by the LB method. They used X-ray diffraction and UV spectroscopy to compare the properties of films first deposited and then polymerised with those first polymerised and then deposited. In many respects they were similar but the films polymerised at the air/water interface had a *d* spacing of 2.9 nm whereas the films polymerised after deposition had a *d* spacing of 3.1 nm. The results of these studies showed that, under both conditions compound **17** will polymerise but there is a residual tilt in the biphenyl groups with respect to the film plane when the polymerisation is carried out at the air/water interface which is not present in the other case. One can not be certain, but it seems likely, that both polymerisation and cross linking take place within a monolayer rather than between monolayers.

Bardosova *et al* [25] studied a chiral compound, **19**, the structure of which is shown in Figure 7. DSC showed that it changed from a crystalline phase to a smectic phase at 43 °C and underwent a further phase change at about 106 °C finally melting at 122 °C. There was considerable thermal hysteresis apparent on cooling. It was possible to deposit this compound by the LB method. At a surface pressure of 15 mN m^{-1} Z deposition (on the upstroke only) took place and X-ray diffraction gave a *d* spacing of 3.7 nm. At 19 mN m^{-1} it was possible to bring about reasonably good Y deposition but X-ray diffraction indicated the presence of three phases having *d* spacings of 3.7 nm, 4.5 nm and 5.0 nm, the first of these phases predominating. The values of these surface pressures were critical and it is interesting to note that between 15 and 19 mN m^{-1} deposition was not possible. These authors also deposited films of this compound by thermal evaporation *in vacuo*. Their results were too complex to discuss here. However it is interesting to note that films evaporated directly from the solid phase and films evaporated from material which had been held at a temperature above the crystal to smectic phase change had different properties. The latter films were initially homeotropic when viewed under the polarising microscope and X-ray diffraction fails to show any Bragg peaks. However, after storage for several hours, Bragg peaks corresponding to a *d* spacing of 2.7 nm appear! These results, while difficult to explain in detail, show how important it is to carry out proper structural studies on films deposited by the LB method.

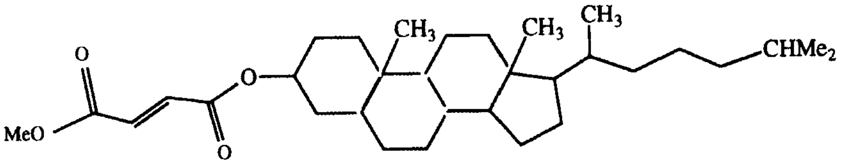


FIGURE 7 The chiral compound studied by Bardosova *et al* [25]

In an effort to produce compounds analogous to **17** but incorporating a triple bond rather than a double bond in the tail unit Bardosova *et al* [26]synthesised a number of compounds the properties of which are discussed in that paper. The closest analogue of **17** which contained an isopropyl fumarate ester and a triple bond in the tail, **20**, underwent a crystal to smectic phase change at 57 °C. However it was very difficult to form good regular layer structures of this compound. The structure of the most interesting member of this family of compounds, **21**, is shown in Figure 8. It was possible to deposit it by the LB method in the Z mode at an optimum surface pressure of 17 mN m^{-1} and also to form films of it by thermal evaporation *in vacuo*. The latter films initially showed neither a 2D crystal structure nor Bragg peaks but, after storing them for several days, they then re-organised themselves and resembled films of this compound formed by the LB method. They consisted of 2D crystallites and gave four Bragg peaks corresponding to a *d* spacing of 2.7 nm. When multilayers formed by either method were heated so as to attain the smectic phase and were then exposed to UV light for 15 minutes in nitrogen they formed films that were insoluble in hot THF and had thus, presumably, been polymerised. However such films gave no Bragg peaks and were thus, disordered Furthermore they did not adhere to the substrate as well as does compound **17** and tended to fall of in the THF as thin flakes.

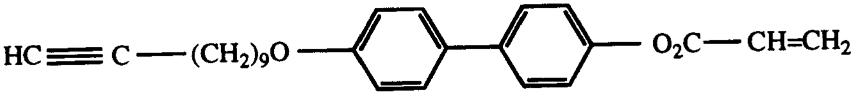


FIGURE 8 The compound, **21**, studied by Bardosova *et al* [26]

TRANSFERRED FREELY SUSPENDED FILMS. (TFS)

There are many papers dealing with films of liquid crystals suspended across small apertures and which are thus supported only at their edges. A majority of these papers discuss films consisting of a relatively large number of monolayers and are thus of no concern to us in the present context. Of particular interest are ultra-thin films which initially bridge an aperture but which are then deposited onto a solid planar substrate. Decher and his collaborators [17,18,27,28,29] developed this method of forming ordered ultra-thin films. A schematic diagram of the apparatus used is shown in Figure 9. The critical aperture is made in a thin sheet of glass or metal (though very little information about this important point appears in any of the papers cited above). The whole apparatus is contained in an enclosure the temperature of which is controlled so as to maintain the compound under study in the smectic phase which it is desired to study. A quantity of the compound is drawn across the aperture and allowed to anneal though, here again, the authors have published very little detail of how this process is carried out or how the final thickness of the film is determined. When a stable film has been obtained the air pressure on the lower side of the film is reduced so that the film collapses onto a substrate placed immediately under the aperture.

Overney *et al* [18] compare the properties of films of compounds **7, 8** and **10** deposited by the transferred freely suspended (TFS) method and by the LB technique. In only one case, compound **10**, were layer spacings compared for multilayers deposited by both methods and then the results, which corresponded to the length of a single molecule, agreed to within the experimental error. AFM studies showed one significant contrast between films formed by these two methods. LB films had steps on their surfaces corresponding to a bilayer whereas films formed by TFS had steps corresponding to a monolayer. These authors propose a possible, though somewhat speculative, theory to account for this result. The TFS method does not require that the molecules involved should be amphiphilic and Decher *et al* [29] have studied very thin films formed from such molecules by this method. This work is of less relevance to our present topic but it is interesting to note that both freely suspended and TSF films exhibited reversible phase changes corresponding to the phase changes which take place in the bulk material.

Decher and his collaborators [17,30] made a special study of compound **7** and compared the properties of multilayers of this compound made by the LB and by the TFS methods. The films made by the former method showed, on heating, one irreversible phase change at 64 °C and started to melt at 80 °C. Films formed by the latter method have a change to the smectic E phase at 70 °C and to smectic B at 87 °C, finally melting at 110 °C. These authors propose that this behaviour can be accounted for by the occurrence of far fewer defects in films formed by TFS as compared with the LB method. Reibel *et al* [30] made a comparison of the structures, at room temperature, of bulk specimens of compound **7** and of films formed by TFS. They found that the structure of TFS films was dependent on the nature of the substrate and was a "frozen in" high temperature phase and did not correspond to the normal bulk phase. The thinnest films which these authors could make using this compound and the TFS method consisted of 7 monolayers.

There is, of course, an extensive literature concerned with the properties of liquid crystal films stretched across apertures most of which is only of peripheral relevance in the present context. However it is interesting to note that Cheng *et al* [31,32] and Geer *et al* [33] were able to form free standing films consisting of as few as two or three monolayers and to characterise them using electron diffraction.

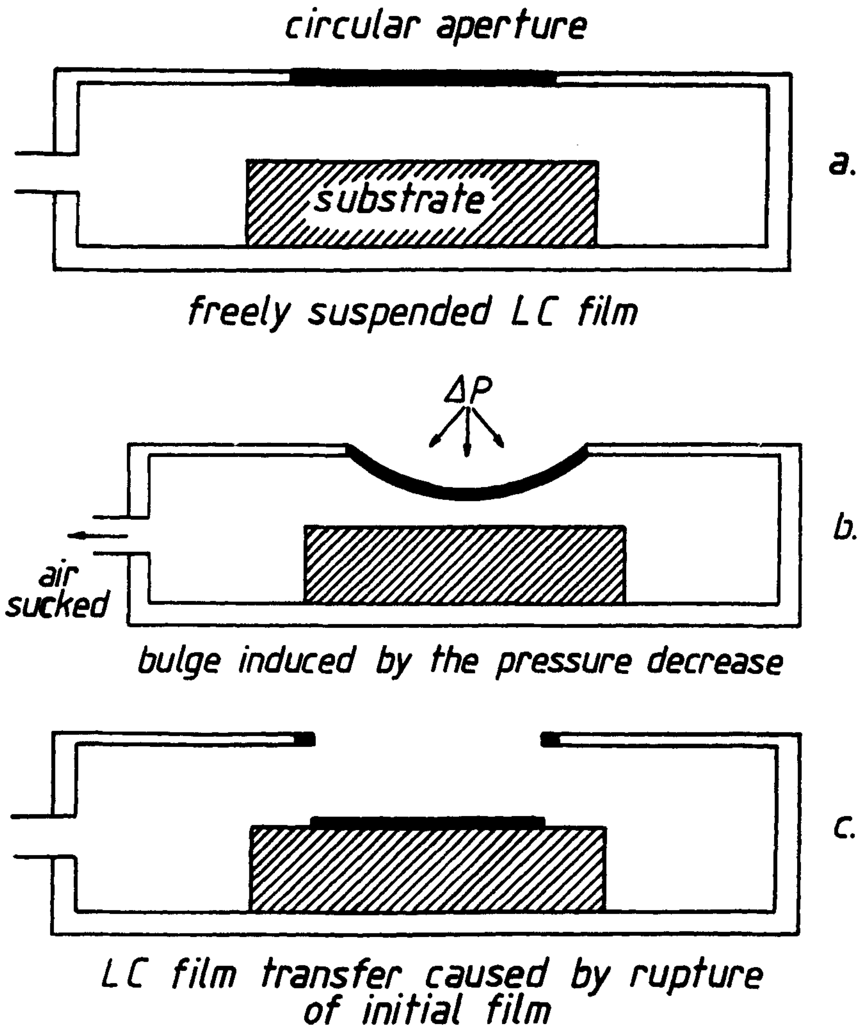


FIGURE 9 Transferred freely suspended films. A schematic diagram showing the method developed by Decher and his collaborators [17,18,27,28,29]. The whole apparatus is contained in a temperature controlled box. *a* shows a vessel having an aperture at the top across which a film of the compound under study drawn. *b* shows the partial collapse of the film as the pressure below it is reduced. *c* shows the deposition of the film onto a suitable substrate as the film ruptures

DISCUSSION

It is clear from the facts related above that compounds which are capable of forming liquid crystals and which can also be deposited by the LB method can only be deposited in this manner at a temperature below the crystal to smectic phase change. On the other hand it is possible to heat LB multilayers of such compounds to above this phase change and obtain structures closely resembling the smectic structures observed in bulk samples. Thin multilayers of such compounds can also be formed by the transfer of freely suspended films onto solid substrates at temperatures corresponding to one of the smectic phases. The crystal structures of multilayers formed in this way when observed at temperatures corresponding to the crystal phase may differ from those observed in normal bulk material and probably arise from the "freezing in" of high temperature structures. This behaviour is only observed in the case of relatively thin films.

Also, as was explained above, it is possible to photo-polymerise thin films of compounds in the smectic phase so as to preserve a homeotropic structure at room temperature. Thus structures which are in equilibrium at temperatures substantially above the crystal to smectic phase change can be partially stabilised, either by the influence of the solid substrate or by photo-polymerisation. In such cases the crystalline film which is formed, though clearly not a liquid crystal, preserves much of the molecular arrangement of the smectic phase from which it originated.

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