Molecules for Langmuir-Blodgett Film Formation [and Discussion]

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Molecules for Langmuir–Blodgett film formation

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Molecules with an appropriate balance between hydrophilic and hydrophobic character may be spread as monolayers on the water surface. Under appropriate conditions these monolayers may be built up onto a substrate as Langmuir–Blodgett (LB) films. This paper reviews the types of molecule that are known to give good LB film formation, with especial reference to potential applications in molecular electronics.

Introduction

The surface of a liquid always has excess free energy, which is due to the difference in environment between surface and bulk molecules; the resultant surface tension (γ) is given by the partial difference (see, for example, Gaines 1966).

$$\gamma = (\partial G/\partial s)_{T,P,n_i},$$

where G is the Gibbs free energy of the system, s is the surface area, and the temperature T, pressure P and composition n_i are held constant. Water has an exceptionally high surface tension of 73 mN m^{-1}. When a monolayer is spread on the water surface, it reduces the surface tension by an amount known as the surface pressure, Π.

$$\Pi = \gamma - \gamma_0.$$

Typical monolayer forming materials such as stearic acid (figure 1) have two distinct regions: a hydrophilic headgroup and a hydrophobic tailgroup, the overall molecule being amphipilic. A solution of stearic acid in chloroform, dropped onto a water surface, spreads to cover the available area and after evaporation of the solvent leaves a sparse monolayer of molecules lying flat on the water's surface (figure 2*a*). If the surface area is now reduced by contraction of a movable barrier system, a number of phase changes are observed. The first occurs as domains of molecules have to approach sufficiently closely for the tail groups to leave the water (figure 2*b*) and subsequently as the molecules become close packed on the surface (figure 2*c*). The surface-pressure–area isotherm (figure 3) shows these phase changes, the first in the inset portion, the second at approximately 0.20 nm^2 per molecule. At areas lower than this, the monolayer is usually taken to be in a solid state; the slope of the line represents the compressibility of the solid and the intercept of its extrapolation represent the (hypothetical) surface area of an uncompressed upright molecule. At smaller areas the films collapse often by a process of multilayer formation (figure 4).

Monolayers on the water surface are frequently termed Langmuir films in honour of the pioneering investigations done by this great scientist (Langmuir 1917), although he was by no means the first to note or indeed study these phenomena (see, for example, Pockels 1891).

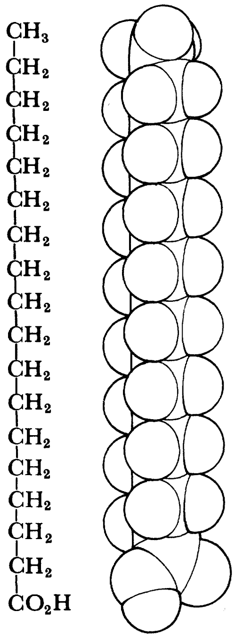

FIGURE 1. Stearic acid (octadecanoic acid).

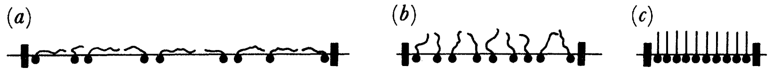

FIGURE 2. Insoluble monolayer (Langmuir film) on a water surface (a) as spread, (b) during compression, (c) after compression to a two-dimensional solid.

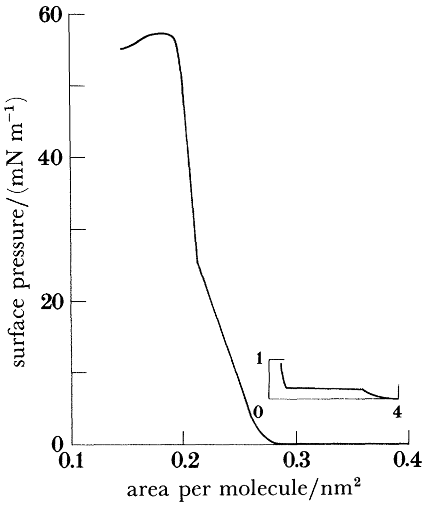

FIGURE 3. Surface-pressure–area isotherm of stearic acid.

Langmuir's assistant Blodgett made the first systematic studies of the deposition of monolayers from the water surface onto substrates (Blodgett 1935). The deposition of such Langmuir–Blodgett (LB) films onto a hydrophilic substrate requires the surface pressure to be controlled to a constant value, and is illustrated in figure 5. No deposition occurs on the first immersion, but as the substrate is withdrawn, the upturned meniscus is wiped over the substrate and

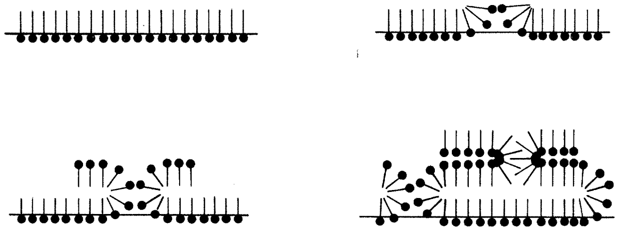

FIGURE 4. Progressive stages of film collapse.

deposits a monolayer with headgroups oriented towards the substrate (figure 5*b*). Drainage of the aqueous film between monolayer and substrate is an important factor normally limiting the maximum rate of monolayer deposition to about 1 mm s^{-1}.

The second immersion into the subphase (figure 5*c*) differs from the first in that the substrate now has a hydrophobic surface, so that the meniscus turns down and a second layer is deposited with headgroups outermost. Continuing the process of removal and immersion leads to successive deposition of layers of alternate orientation. This process is known as *Y*-type deposition.

Some molecules will deposit only on immersion (*X*-type deposition) or on removal from the subphase (*Z*-type deposition). It might be expected that the resultant LB films would have the *X*, *Y* and *Z* structures illustrated in figure 6. However, simple fatty acids always rearrange to

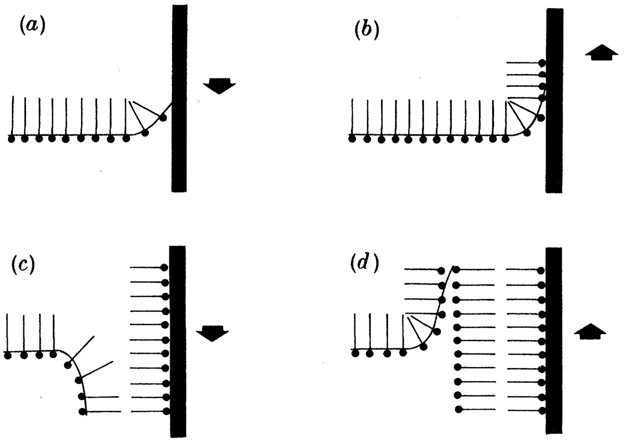

FIGURE 5. Langmuir–Blodgett deposition (see text for detailed discussion).

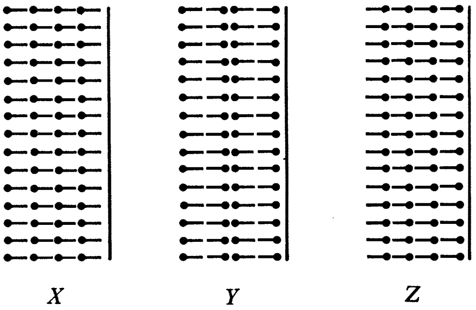

FIGURE 6. *X*-, *Y*- and *Z*-type multilayers.

a *Y* structure, irrespective of the mode of deposition. More rigid molecules will retain their orientation to some extent, although the structure of *X* or *Z* films is usually less perfect than that of *Y* films.

MOLECULES THAT FORM MONOLAYERS

The early work by Langmuir and Blodgett and others (see, for example, Adam & Dyer 1924) was almost exclusively concerned with the fatty acids and closely related compounds. However, although these are good LB film formers their properties are generally uninteresting; for example they have no visible or near-ultraviolet (UV) absorption or emission spectrum, they are electrical insulators and they do not readily polymerize. The insulation properties can, however, be used in the fabrication of capacitors, which in turn can be a useful means of characterization of the LB films. Typically, the films are deposited onto an aluminized glass substrate and gold electrodes are vacuum deposited onto the top of the film. The capacitance is inversely proportional to the film thickness so a plot of the inverse of capacitance against the number of layers deposited yields a straight line (figure 7).

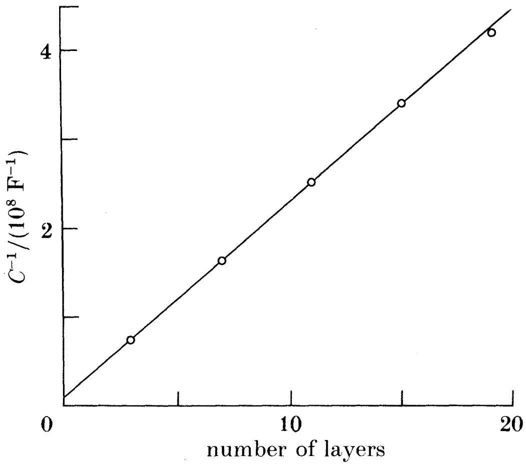

FIGURE 7. Variation of the capacitance of cadmium arachidate LB films with the number of deposited layers, plotted as the inverse of the capacitance against the number of layers.

Many simple long-chain derivatives have been spread as monolayers on the water surface provided that the molecule has a hydrophilic headgroup and a straight carbon chain of at least fourteen atoms, these monolayers are stable for long periods unless the headgroup is fully ionized in which case micelles are formed. However, only a few materials can be successfully deposited as LB films; for example the fatty alcohols cannot be deposited although their surface-pessue–area isotherms closely resemble those of the corresponding fatty acids.

Introduction of a double bond into the carbon chain reduces the linearity of the molecule, most significantly if the double bond has the *Z* configuration as in oleic acid (figure 8) in which the isotherm is much more highly expanded than that of stearic acid (Adam & Dyer 1924). The corresponding E isomer, elaidic acid (figure 9), not only looks more compact, but has a surface area per molecule intermediate between that of oleic and stearic acids (Alexander 1939). The influence of molecular shape on packing is also shown up by the melting points of the three acids (stearic, 70 °C; eleidic, 52 °C; oleic, 14 °C).

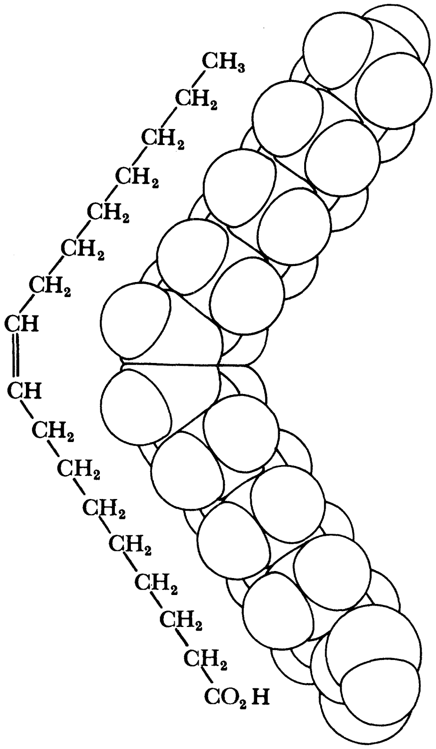

Figure 8. Oleic acid.

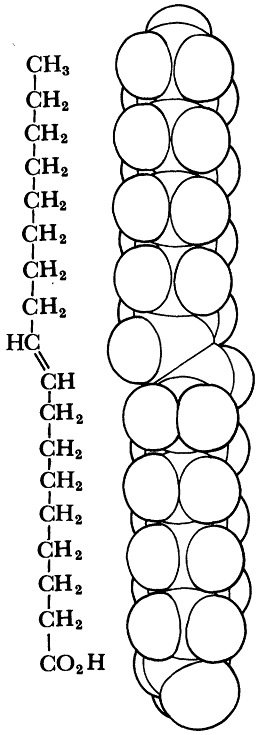

Figure 9. Elaidic acid.

Disruption of the structure is minimized if the double bond is at the end of the hydrocarbon chain as in 22-tricosenoic acid (figure 10), although the residual disruption of packing is probably responsible for this molecule's ability to undergo rapid deposition (Peterson *et al.* 1983). If triple bonds are introduced into the chain, the resulting molecules (see, for example, figure 11) often form compact monolayers that can readily be built up into LB films (Tieke

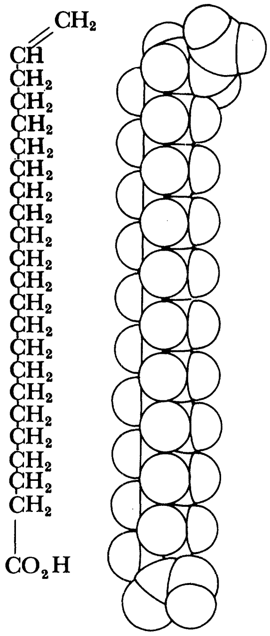

Figure 10. 22-Tricosenoic acid.

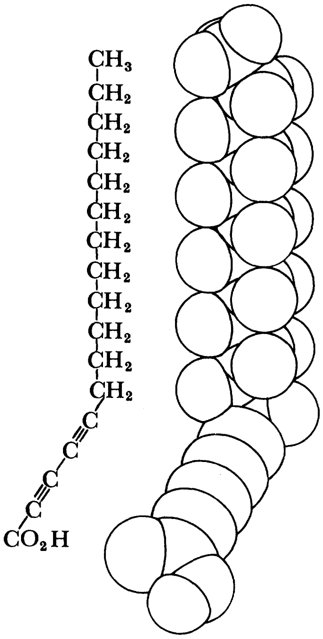

Figure 11. Heptadecadiynoic acid.

et al. 1977). It is most likely that the rigid diacetylene groups control the packing of the monolayer and LB films.

OPTICAL PROPERTIES OF LB FILMS

The first major breaking away from the simple fatty-acid derivatives was in the work of Kuhn & Möbius (Kuhn & Möbius 1971). They pioneered the preparation and deposition of long-chain substituted dye molecules (such as in figure 12). These were deposited as mixed layers with fatty acids and allowed processes such as optical absorption, fluorescence and energy transfer to be studied under conditions where the environment (especially molecular separation) was extremely well controlled.

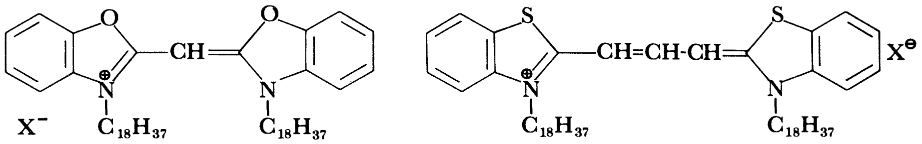

FIGURE 12. Cyanine dyes substituted for LB deposition.

More recent interest in the optical properties of LB films has centred around their nonlinear optical (NLO) behaviour. The particular significance of LB films is because of the requirement for non-centrosymmetry if a material is to show a second-order optical nonlinearity. The structures showing large molecular second-order effects normally involve an electron donating and an electron withdrawing group placed at opposite ends of a π-electron system, and therefore tend to have large dipole moments. These dipole moments usually dominate the crystal packing and ensure that the macroscopic second-order coefficient $\chi^{(2)}$ is zero.

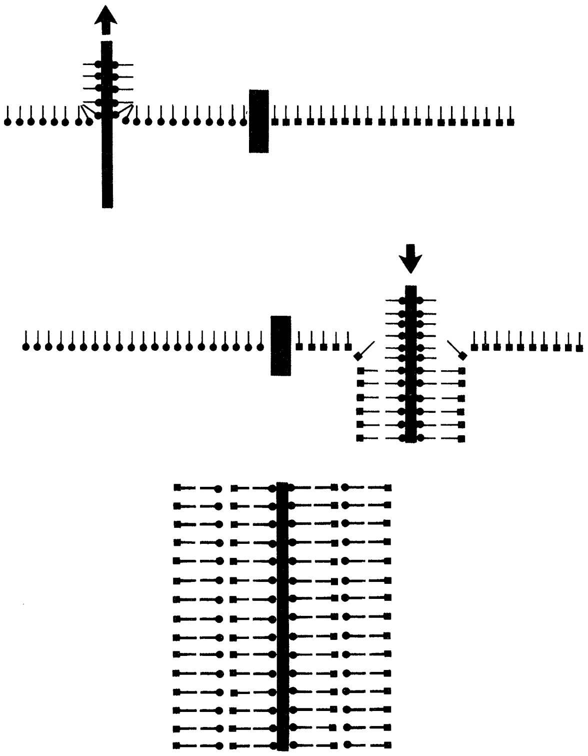

FIGURE 13. Alternate layer deposition.

LB deposition naturally allows production of ordered arrays of aligned molecules. However, *Y*-type deposition leads to a centrosymmetric structure (figure 6) in which the effects of one layer are cancelled by the next layer. This can be overcome, either by the use of *X*- or *Z*-type deposition, which can be forced by appropriate control of surface pressure during deposition (see, for example, Ledoux *et al.* 1987), or by deposition of alternate layers of two different materials (figure 13) to give an LB film with the desired overall optical asymmetry (see, for example, Girling *et al.* 1985). Some NLO molecules are shown (figure 14), where the basic π-electron structure has been modified for deposition usually by the addition of a carboxylic acid group at one end of the molecule and an alkyl chain at the other end. Pyroelectric behaviour also requires a non-centrosymmetric structure, and alternate films have been studied in this context (see, for example, Jones *et al.* 1988).

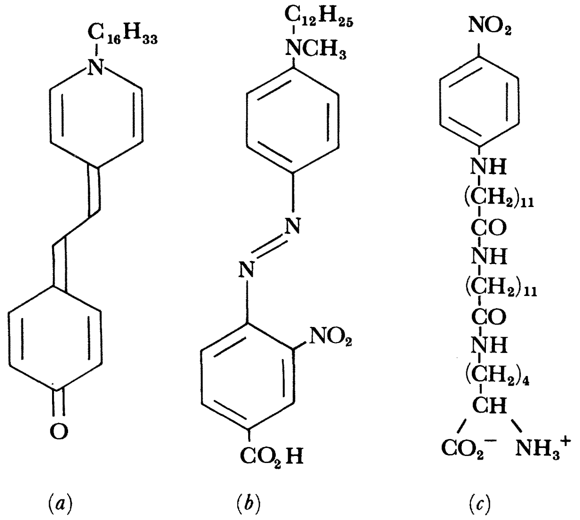

FIGURE 14. Hydrophobically substituted dyes showing nonlinear optical activity.

In general, *X*- or *Z*-type films have lower stability than *Y*-type, because of the relatively unfavourable head to tail interactions in the layers. However, it has been reported that if the hydrophobic tail is substituted with an amide group it is possible to make materials which naturally form *Z*-type multilayers. For example, the long-chain amide (figure 14*c*) is reported (Popovitz-Biro *et al.* 1988) to form stable *Z*-type multilayers, the quality of which is indicated by the almost quadratic dependence of second harmonic generation on the number of layers.

ELECTRICALLY CONDUCTIVE LB FILMS

The first attempt to make LB films with significant electrical conductivity was based on derivatives of anthracene in which the length of the hydrocarbon chains was minimized (see, for example, Steven *et al.* 1983) by careful balancing of the hydrophilic and hydrophobic parts of the molecule. The most lightly substituted molecule to give stable films and LB multilayers is shown in figure 15. Built up films of up to 500 layers were prepared and were found to have a moderate in plane conductivity of $10^{-10}\ \Omega^{-1}\ m^{-1}$ and a much lower conductivity of $10^{-18}\ \Omega^{-1}\ m^{-1}$

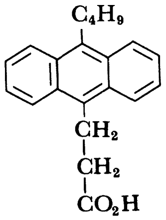

FIGURE 15. Butylanthrylpropanoic acid.

normal to the plane. Photoconductivity and electroluminescence were also observed (Barlow *et al.* 1979).

This anisotropy is commonly observed in LB films of many compounds because the layers are separated by electrically inactive alkyl chains (even when these are short, as in the anthracene derivative of figure 15). Attempts to make highly conductive LB films have mainly centred around the preparation of multilayers containing charge-transfer complexes. For example, the docosylpyridinium salt (shown in figure 16) on doping with iodine gave a conductivity of $10^{-3}\ \Omega^{-1}\ m^{-1}$ (Ruaudel-Teixier *et al.* 1985). Several tetrathiafuluene (TTF) derivatives (see, for example, figure 17) also show high conductivity on doping with iodine (Dhindsa *et al.* 1989), although the long alkyl chains guarantee that the through-film conductivity will be low.

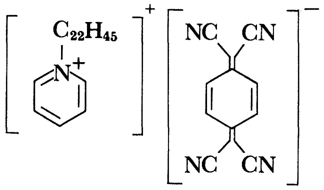

FIGURE 16. Docosyl pyridinium tetracyanoquinodimethane (TCNQ).

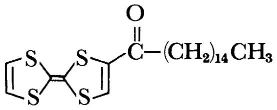

FIGURE 17. Stearoyl TTF.

A recent attempt to make a less anisotropic conductor involved the deposition of the conductive polymer poly(phenylene vinylene) by using the scheme outlined in figure 18. The polyionic precursor polymer (figure 18*a*) was deposited as LB films, which were then converted thermally to the desired polymer (figure 18*b*). When the films were doped with sulphur trioxide the in-plane conductivity was $5 \times 10^{-3}\ \Omega^{-1}\ m^{-1}$ and the through film conductivity was $4 \times 10^{-8}\ \Omega^{-1}\ m^{-1}$. This marked anisotropy even in the absence of insulating spacer groups is

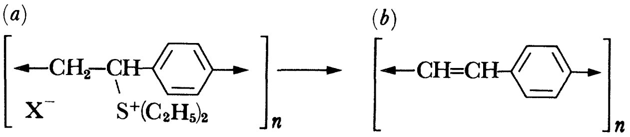

FIGURE 18. (*a*) Surface active precursor ($X^- = C_8F_{17}CO_2^-$) and (*b*) poly(phenylenevinylene).

probably due to the difference between in-chain conduction and hopping between different polymer chains (Nishikata *et al.* 1988).

Another approach to moderately conductive LB films has made use of the special properties of porphyrins and phthalocyanines. These macrocyclic molecules are of particular interest because of their ability to chelate a wide range of metal ions, which then modify the electronic properties of the molecule as a whole. The phthalocyanines are of greatest interest because many of these molecules are unusually stable to chemical attack and it also happens that LB films of the tetra-*tert*-butylphthalocyanines (TBP) (figure 19) are exceptionally stable mechanically (Baker *et al.* 1983). Copper TBP, for example (figure 19, M = Cu) can be spread as monolayers and deposited as multilayers with an in-plane conductivity of $10^{-4}\ \Omega^{-1}\ \mathrm{m}^{-1}$, with a through-plane conductivity apparently only one order of magnitude lower. The molecules appear to be arranged in parallel stacks on the waters surface and a single monolayer has been imaged by transmission electron microscopy (Hann *et al.* 1985). Because of their chemical stability and the ability to include a wide range of metal ions, phthalocyanine LB films, are particularly attractive as chemical sensors. Various groups have examined this application (see, for example, Lloyd *et al.* 1988).

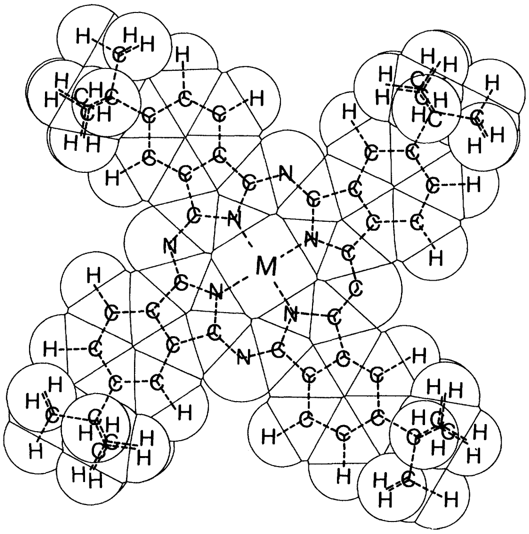

FIGURE 19. Tetra-*tert*-butylphthalocyanine.

Most measurements of LB film conductivity are concerned with in-plane conduction. There are two main reasons for this: firstly, the most common substrates for deposition are either insulators (e.g. glass) or aluminium (which forms an insulating oxide film). It is relatively easy to make good contact to the top of a film on an insulator by vacuum deposition of gold electrodes. Study of through-plane conduction requires less-easy deposition onto a conductive oxide or the preparation of, for example, hydrophilic gold films under especially clean conditions. A further problem is caused by the tendency of gold top electrodes to form conductive whiskers through the film.

A high proportion of samples is therefore unusable except where the LB films are hundreds of layers thick, although recent work on other top electrodes has indicated that it is possible to make good measurements on very thin samples (Geddes *et al.* 1988, 1989).

Polymerizable LB films

One of the attractions of the phthalocyanine films discussed above is their stability to temperature and abrasion. LB films in general are rather delicate structures not only because they are thin but also because the molecular arrangement is usually higher in energy than that of a crystal. One way of increasing the stability of the layer structure is to build the individual molecules into a polymer chain. Perhaps the most generally useful method is the deposition of preformed polymers, which is discussed by P. Hodge (this Symposium). However, polymerizable LB films are of interest as they allow the study of systems inaccessible as preformed polymers, and also because they often can be selectively polymerized by exposure to an electron beam and thus patterned for possible use as a resist.

Polymerization in LB films is hampered by the volume change inherent in many reactions. Vinyl polymerizations show a very significant contraction, and it has been shown in the case of 22-tricosenoic acid (figure 10) which has been extensively studied as a resist material, that the chain length of the polymer is limited by the shrinkage of the growing polymer chain away from neighbouring molecules (Barraud *et al.* 1977).

This problem is avoided in polymerization of the diacetylenes (see, for example, figure 11). However, the requirements for solid-state polymerization dictate that it can only occur within areas of crystalline order, so that the chains are interrupted at the grain boundaries between two-dimensional crystalline domains (Tieke *et al.* 1977). An alternative polymerization route uses the oxiran reactive group, which will polymerize by ring-opening to give a minimal volume change. Various long-chain epoides have been deposited and polymerized (figure 20) by electron beam exposure (Boothroyd *et al.* 1985).

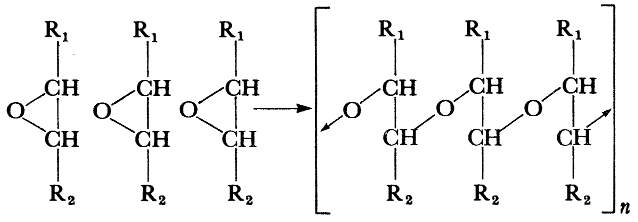

FIGURE 20. Oxiran polymerization.

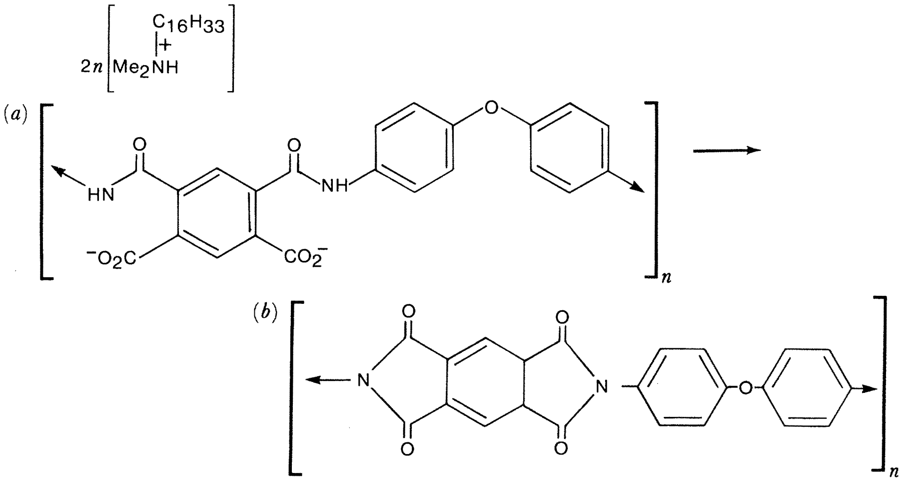

FIGURE 21. (*a*) Precursor polymer; (*b*) polyimide.

It is sometimes possible to deposit polymers that are precursors to the final film in a similar way to the scheme illustrated in figure 18. For example, the precursor in figure 21*a* can be converted on heating to the extremely tough polyimide of figure 21*b*. As the layer thickness of the final material is only 0.4 nm, it is surprising that no disruption occurs on elimination of the bulky counterions (Kakimoto *et al.* 1986). An alternative route to this and similar materials has been studied by Uekita *et al.* (1988).

Molecular electronics application of LB films

Many of the properties already discussed are of potential significance for molecular electronics, for example the anistropic conductivity, pyroelectric, linear and nonlinear optical properties. A large number of these properties have already been investigated in connection with sensors (see, for example, the review by Moriizumi (1988)).

LB films are of particular value where it is essential to control molecular orientation, such as in materials for second-order nonlinear optics. Indeed it is probably easier to evaluate a new π-electron system by attaching suitable groups and by depositing LB films than it is by any other method. Conversely, one of the great difficulties with LB films is the preparation of thick layers, as this involves time-consuming repetitive coating procedures. One area where LB films are naturally suited is the modification of surfaces and interfaces, for example semiconductor surfaces (Petty *et al.* 1985).

The thermal instability of many LB films is one major obstacle to their application. In this context, the deposition of polymeric materials as discussed by P. Hodge (this Symposium) is of paramount importance.

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Discussion

P. KATHIRGAMANATHAN (*Cookson Group p.l.c., Middlesex, U.K.*). Why are LB-film-based sensor devices not in the market yet?

R. A. HANN. The technology of LB deposition is not sufficiently well advanced to allow preparation of films on a commercial basis.