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MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

# Preformed Polymers for Langmuir-Blodgett Films [and Discussion]

P. Hodge, F. Davis, R. H. Tredgold, J. Silver and H. J. Coles

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# Preformed polymers for Langmuir–Blodgett films

By P. Hodge[1]†, F. Davis[1] and R. H. Tredgold[2]
[1] Department of Chemistry and [2] Department of Physics, University of Lancaster,
Lancaster LA1 4YA, U.K.

Langmuir–Blodgett (LB) films of simple molecules are usually fragile and this has prompted the study of polymeric LB films. Films have been prepared successfully from preformed polymers that are derivatives of various vinyl-maleic anhydride alternating copolymers. By using a computer-controlled trough polymeric films containing several hundred layers have been prepared. Low-angle X-ray scattering studies indicate that the films have a regular layer structure. By using a specially constructed trough, multilayers have been prepared in which alternate layers are polymeric. LB films prepared from polymers containing appropriate vinyl groups can be crosslinked by ultraviolet light or an electron beam (EB). This not only further stabilizes the films and renders them insoluble, but also allows patterns to be 'drawn' in the films. Films of these polymers have been used as submicrometre EB resists. Films suitable for second harmonic generation and electro-optic modulation have been prepared. Some further applications of polymeric LB films are outlined.

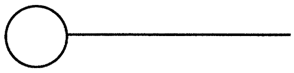
## Introduction

It has been known for many centuries that when oil is placed on water it spreads out to form exceedingly thin films. Some of the most well-known experiments of this kind are those carried out on the ponds at Clapham by Benjamin Franklin, who described the experiments in this journal 215 years ago (Franklin 1774). Such studies were greatly extended by Agnes Pockels in the 1890s (Pockels 1891, 1892, 1893, 1894). In addition to studying oils, she studied films of stearic acid **1***a*:

$$CH_3(CH_2)_{16}CO_2H$$

**1***a*

Films of this important molecule and others were later studied extensively and systematically by Irving Langmuir (1917, 1920). Stearic acid is of particular interest because the molecules have a part (the $—CO_2H$ group) that is attracted to water (hydrophilic) and a part (the $C_{17}$ hydrocarbon chain) that is repelled by water and attracted by oil (lipophilic). Such molecules, which have both hydrophilic and lipophilic parts, are called amphiphiles. They are extremely important in interfacial systems, especially in Nature. It is convenient to represent the hydrophilic and lipophilic parts of amphiphiles by circles and lines respectively. Stearic acid, for example, can be represented as in **1***b*:



**1***b*

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† Present address: Department of Chemistry, University of Manchester, Manchester M13 9PL, U.K.

The behaviour of water-insoluble amphiphiles at an air–water interface is usually monitored by using a Langmuir trough. This is a piece of equipment that includes a clean water surface the area of which can be precisely adjusted by barriers while the surface pressure of a monolayer introduced onto the water surface can be measured accurately. Hence a pressure ($\pi$) against area per molecule ($A$) isotherm can be determined. A typical isotherm for stearic acid is shown in figure 1. In practice an organic solution of the amphiphile under study is floated on the water surface and the solvent allowed to evaporate. The film so obtained on the water surface is called a Langmuir film. When the area available per molecule is very large the molecules spread out on the surface and produce very little surface pressure. The hydrophilic groups will be in contact with the water; the lipophilic chains will lie mainly on the surface. As the surface area is progressively reduced the hydrophilic groups occupy a larger fraction of the surface available, the amphiphilic molecules increasingly come into contact with each other and the surface pressure increases. Eventually, a point is reached where the hydrophilic groups are in close contact at the water surface and the lipophilic groups are away from the surface and in close contact with each other. The amphiphile is now in the form of a close-packed monolayer. With stearic acid at this stage the lipophilic groups are essentially vertical and in a close packed array (see figure 2) and the surface area per molecule corresponds

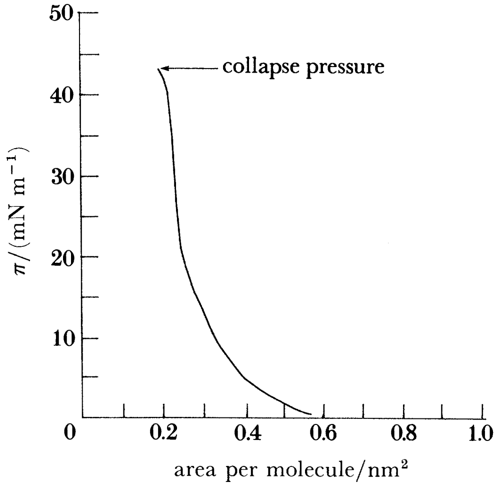


FIGURE 1. Pressure against area per molecule isotherm for stearic acid on water at 20 °C.

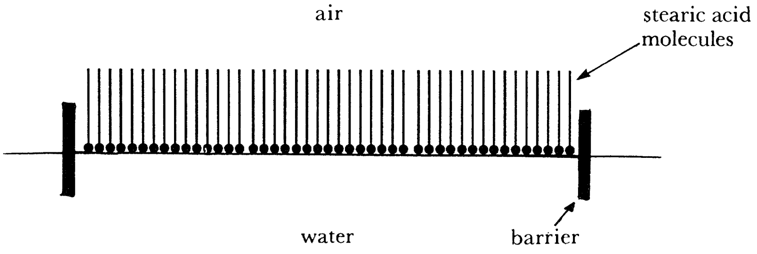


FIGURE 2. Schematic representation of a close-packed Langmuir film of stearic acid on water.

to the cross-sectional area of stearic acid (*ca.* 20 Å$^2$†). Further compression is difficult, but if it is continued a pressure is finally reached at which the film collapses (the collapse pressure).

A further step forward in the study of monolayers resulted from the work of Katherine Blodgett. By systematic study she developed a technique that allows relatively stable Langmuir films to be transferred onto a solid substrate such as glass or quartz (Blodgett 1935). This was achieved by slowly drawing the solid substrate through the monolayer surface while maintaining the surface pressure. In successful transfers the area occupied by the amphiphile on the substrate is essentially the same as that occupied on the water surface. That is the *deposition ratio* (area occupied on substrate to area occupied on water), which is close to 1.0. Repetition of the transfer process results in multilayers. These layers on solid substrates are called Langmuir–Blodgett (LB) films.

Figure 3 gives a schematic diagram of the transfer process where it is supposed that the substrate is initially hydrophilic. In the case where the monolayer is deposited on both upward and downward passages the process is referred to as *Y*-deposition. The multilayer obtained, see figure 4, is in effect a series of bilayers. If deposition only takes place during passage down through the layer, the process is known as *X*-deposition; if only during passage up through the layer, *Z*-deposition. In most cases *X*- or *Z*-deposition results from faulty *Y*-deposition.

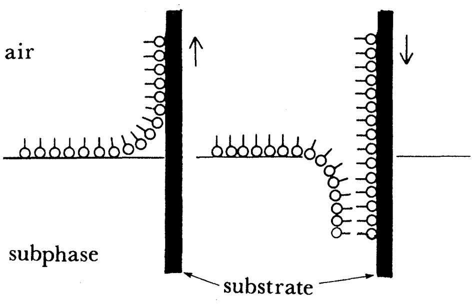
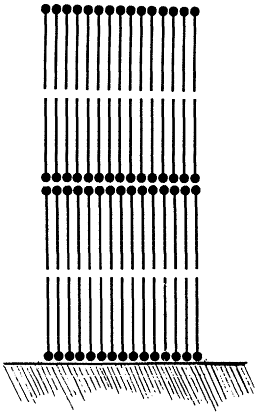


FIGURE 3. Schematic diagram of the transfer process to give a *Y*-type multilayer.



solid substrate

FIGURE 4. Schematic representation of part of an LB film resulting from *Y*-deposition.

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† 1 Å = $10^{-10}$ m = $10^{-1}$ nm.

It should be stressed that the fact that an amphiphile gives a good isotherm and transfers well to give an LB film does not mean that the latter is highly ordered or, if it is, that the molecular arrangement in the multilayer is the same as in the Langmuir film. The regularity of the LB layer structure can often be checked by low-angle X-ray scattering. Thus if a multilayer contains heavy atoms that as a consequence of an ordered structure appear at regular intervals, this will lead to X-ray scattering according to the Bragg equation: see figure 5. With carboxylic acid head groups the presence of cadmium chloride in the aqueous subphase usually leads to LB films that have $Cd^{2+}$ ions at the hydrophilic interface thus facilitating determination of the layer spacings.

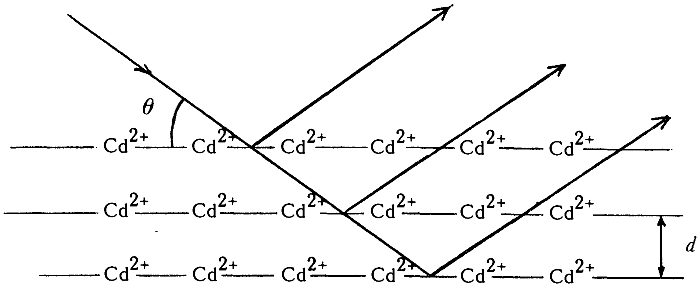


FIGURE 5. Low-angle X-ray scattering resulting from a carboxylic acid LB film prepared over $CdCl_2$. Bragg equation: $2d \sin\theta = n\lambda$, where $n$ is an integer and $\lambda$ is the wavelength of light.

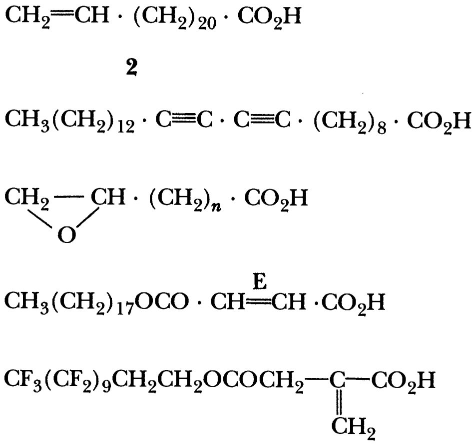
Since Langmuir's and Blodgett's pioneering studies an enormous amount of research has been done on both Langmuir films and LB films. The book by Gaines (1966) is an extremely valuable compilation of early work. Since then reviews have appeared on various aspects (Kuhn *et al.* 1973; Vincett & Roberts 1980; Breton 1981; Roberts *et al.* 1981; Peterson & Girling 1985; Sugi 1985; Roberts 1985; Hodge *et al.* 1985; Tredgold 1987).

## SOME RECENT DEVELOPMENTS

The field of LB films received a major research boost about 10 years ago with the recognition that such multilayers, being ordered at the molecular level, could have applications in molecular electronics and in optoelectronics. Some of these applications have been discussed recently by Roberts (1985). With the resurgence of interest many new organic amphiphiles have been synthesized and studied, the design of troughs has been improved (Roberts *et al.* 1981; Daniel & Hart 1985) and in most equipment now used the LB dipping process is automated and computer controlled (Vickers *et al.* 1985; Dutta *et al.* 1985). This makes the preparation of LB films consisting of several hundred layers a practical proposition. Double-ended troughs are now available that permit the preparation of alternating multilayers (Barraud *et al.* 1985; Daniel & Hart 1985). Despite this progress problems remain. Thus the fabrication of thick multilayers is very time consuming and in general the LB multilayers are not as stable or as robust as is needed for commercial applications.

## Polymeric Langmuir–Blodgett films

It is clear that polymeric LB multilayers should be more stable and robust than those prepared from non-polymeric molecules, though they may not be quite so highly ordered. Two approaches may be used for the preparation of polymeric films. One, extensively studied recently by Ringsdorf's group at Mainz, uses organic amphiphiles that are also monomers (see, for example, Naegele *et al.* 1977; Barraud 1983; Elbert *et al.* 1985; Laschewsky *et al.* 1985, 1988; Frey *et al.* 1987). Once the multilayers have been formed polymerization is initiated by irradiation, most commonly with ultraviolet (UV) light. Examples of polymerizable amphiphiles are shown in scheme 1. The polymerization of ω-tricosenoic acid **2** by electron beam irradiation (Barraud 1983) is of interest because unactivated α-olefins do not normally polymerize so easily. Presumably, the ordering of the olefinic residues facilitates polymerization. Not surprisingly, because polymerization generally results in a contraction in volume, the polymeric films produced using this general approach tend to crack and craze (Lieser *et al.* 1980; Sarkar & Lando 1983), though this is not always the case (Delaney *et al.* 1985; Boothroyd *et al.* 1985; Rabe *et al.* 1985).



$CH_2{=}CH \cdot (CH_2)_{20} \cdot CO_2H$

**2**

$CH_3(CH_2)_{12} \cdot C{\equiv}C \cdot C{\equiv}C \cdot (CH_2)_8 \cdot CO_2H$

$CH_3(CH_2)_{17}OCO \cdot CH\overset{E}{=}CH \cdot CO_2H$

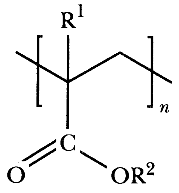
$CF_3(CF_2)_9CH_2CH_2OCOCH_2{-}\underset{\underset{CH_2}{\|}}{C}{-}CO_2H$

Scheme 1. Some examples of polymerizable amphiphiles

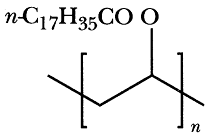
The second approach, and the one with which this article is mainly concerned, is to prepare the LB films directly from preformed polymers. Attractive features of this approach are that no processing of the LB film is needed once it is formed and that certain types of polymers may prove to be suitable vehicles for moieties that will not form good films by themselves.

To obtain good monolayers from preformed polymers it is anticipated that the hydrophilic and lipophilic groups will need to be regularly and frequently spaced along the polymer chain. If this is not the case, when a Langmuir film is formed any blocks of hydrophilic groups will coil up in the aqueous subphase and any blocks of lipophilic groups will coil up above the water surface. LB multilayers prepared from such films would be most unlikely to be highly ordered. Polymers that appear to meet this requirement and that have been studied as Langmuir films include (see table 1 and diagrams below) poly(acrylate)s **3** (Crisp 1958; Winter *et al.* 1985), poly(methacrylate)s **4** (Crisp 1958; Puggelli & Gabrielli 1977; Winter *et al.* 1985), poly(vinyl esters) **5** (Puggelli & Gabrielli 1977), and poly(vinyl ethers) **6** (Lovelock *et al.* 1985). However, in all these polymers the hydrophilic groups (ester or ether) are relatively weakly hydrophilic.

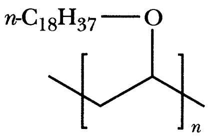
Table 1. Some polymers studied as Langmuir films



| | $R^1$ | $R^2$ |
|---|---|---|
| **3** | H | $n$-$C_4H_9$ and other alkyl derivatives |
| **4** | $CH_3$ | $CH_3$, $n$-$C_4H_9$, $n$-$C_{12}H_{25}$ and other alkyl derivatives |
| **7** | H | $n$-$C_{18}H_{37}$ |
| **8** | $CH_3$ | $n$-$C_{18}H_{37}$ |



**5**



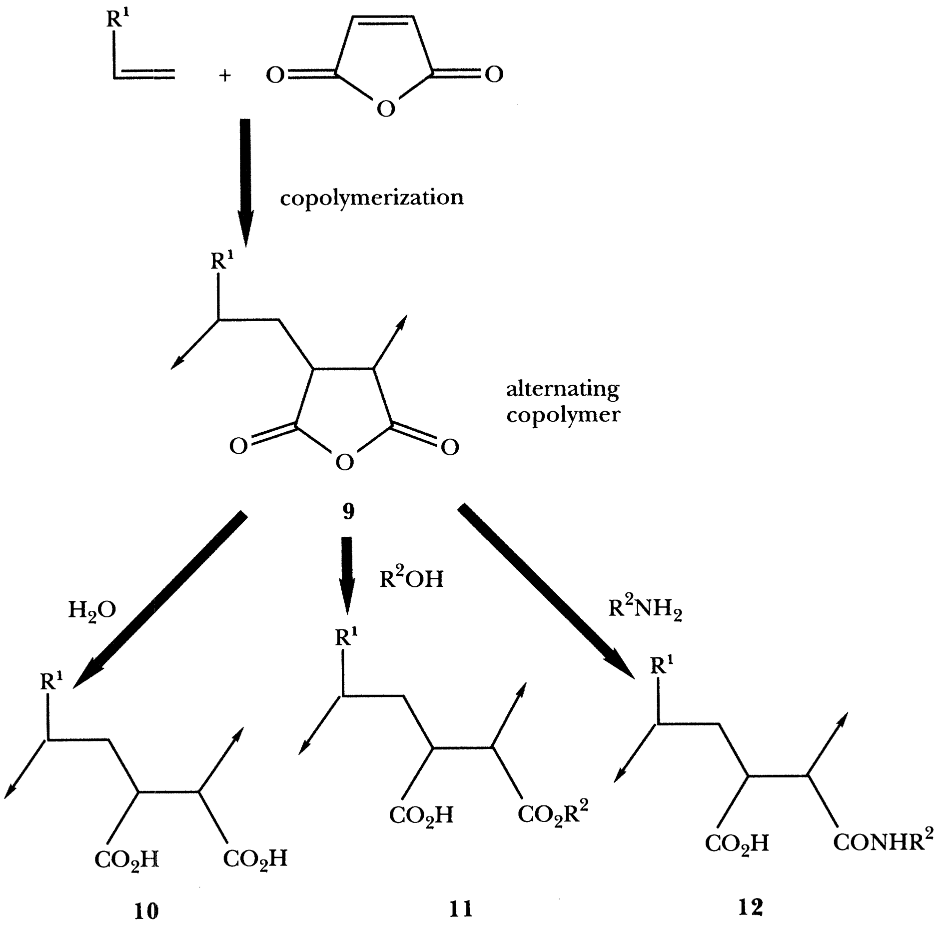
**6**

Even so, Mumby *et al.* (1986) prepared LB films containing a few monolayers of poly(octadecyl acrylate) **7** and of poly(octadecyl methacrylate) **8**. Recently, with great care, ordered LB multilayers (up to 40 layers) of poly($n$-octadecyl methacrylate) **8** have been prepared (Schouten *et al.* 1988).

For the present programme polymers with more powerful hydrophilic groups such as —$CO_2H$ and —$CONH_2$ were sought. Addition polymers prepared by using maleic anhydride are particularly attractive because the anhydride residues present in the products can be reacted with water, ammonia, alcohols or amines to produce the desired hydrophilic groups (see scheme 2). Maleic anhydride does not homopolymerize easily, but it copolymerizes readily with a wide range of α-olefins such as styrene and hexadec-1-ene (see scheme 2). This provides an opportunity to introduce lipophilic groups and because such copolymers generally have a very high degree of alternation the desired regularity of placement of the hydrophilic and the lipophilic groups is assured. $^{13}C$ NMR Spectral studies (Rätzsch *et al.* 1986; Davis & Hodge 1990) of polymers **9** indicate that during copolymerization with propene and with hexadec-1-ene addition across the carbon–carbon double bond of maleic anhydride is approximately 80% *trans* and 20% *cis*. When the copolymers react with methanol the proportions of the two possible half ester moieties is approximate 60:40.

The initial work with such polymers, carried out by Tredgold & Winter (1982), involved poly($n$-octadecylvinyl ether-co-maleic anhydride), poly(octadec-1-ene-co-maleic anhydride), and poly(styrene-co-maleic anhydride). Layers of these polymers were spread on water and the anhydride residues allowed to hydrolyse. The Langmuir films so obtained were transferred as monolayers onto Al–$Al_2O_3$ coated microscope slides. These were the first LB films prepared from preformed polymers.

Later work on polymers of this type involved derivatives (see scheme 2) of styrene-maleic anhydride copolymers. Because this work has been reviewed in some detail (Hodge *et al.* 1985) it will not be discussed in detail here. In summary, while the polymers formed monolayers that displayed good isotherms, the LB multilayers prepared from them on glass substrates coated with Al–$Al_2O_3$ were not generally highly ordered in that when investigated by low-angle X-ray scattering at best they showed just one Bragg peak (Tredgold *et al.* 1985; Jones *et al.* 1985).



Scheme 2. Polymer syntheses

Various pieces of evidence (Hodge *et al.* 1985; Jones *et al.* 1987) suggest that the polymers were organized in the Langmuir films as shown in figure 6.

More recently polymers have been studied that are derivatives (see scheme 2) of maleic anhydride and simple long chain α-olefins (Winter *et al.* 1985; Davis & Hodge 1990). Treating the copolymers **9** ($M_n$ 2500–37000) prepared from maleic anhydride and a series of olefins $CH_3(CH_2)_nCH{=}CH_2$, with water, methanol, ethanol, 2,2,2-trifluoroethanol, ammonia, dimethylamine, or morpholine gave polymer derivatives which formed excellent LB multilayers

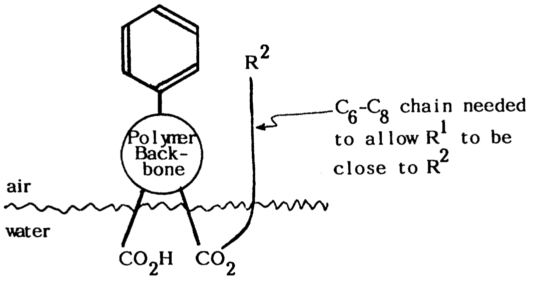


Figure 6. Schematic representation of a Langmuir film of alcohol ($R^2OH$) derivatives of a styrene–maleic anhydride copolymer.

(two or more Bragg peaks) providing $n \geqslant 5$. In each case the area per alternating repeat unit was 32–37 Å$^2$ at surface pressures of 30 mN m$^{-1}$. In the LB films (deposited on silicon) the thickness per bilayer increased regularly with the value of $n$ and suggested the lipophilic chains were tilted at an angle of about 45° to the plane of the substrate. All the available evidence suggests that the LB multilayers have the form shown schematically in figure 8 (Davis & Hodge 1990).

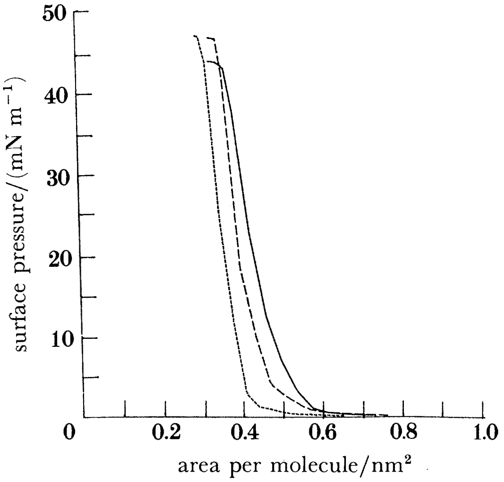


FIGURE 7. ———, Isotherms of polymer 15; ------, polymer 16; ——, polymer 17.

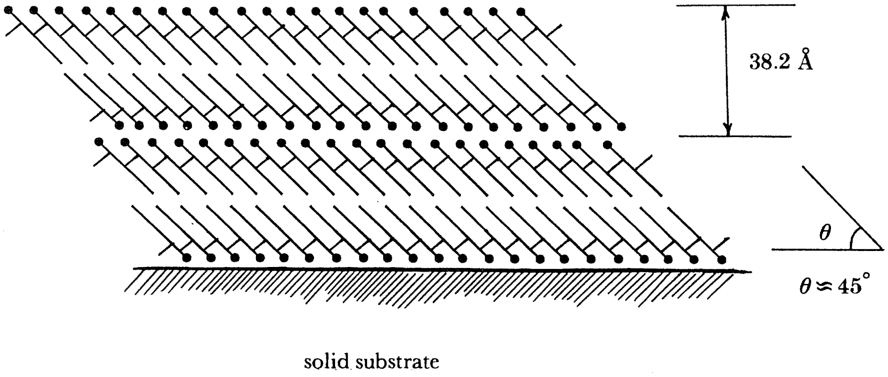


FIGURE 8. Probable arrangement of multilayer of octadec-1-ene-maleate half methyl ester copolymer.

In an attempt to improve packing and stability polymers were prepared by using α-olefins containing mesogenic groups. Although excellent Langmuir films may be prepared from cholesterol **13**, LB multilayers are not easily obtained. However, the polymer **14**, containing a cholesteryl unit, formed a stable regular LB multilayer (bilayer spacing 34.4 Å) illustrating the ability of the polymers to assist in the formation of stable multilayers (Davis & Hodge 1990).

Biphenyls are one of the commonest mesogens and the use of α-olefins containing such mesogens allowed the preparation of polymers such as **15**, **16** and **17**, which formed satisfactory multilayers on silicon (Davis *et al.* 1990). Isotherms for these polymers are shown in figure 7.

In recent years LB films have been prepared from preformed polymers by other research groups (see, for example, Elbert *et al.* 1985; Nishikata *et al.* 1988; Watanabe *et al.* 1988).

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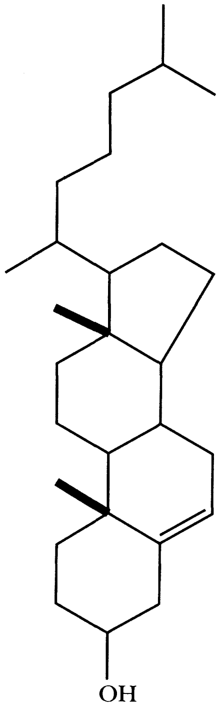
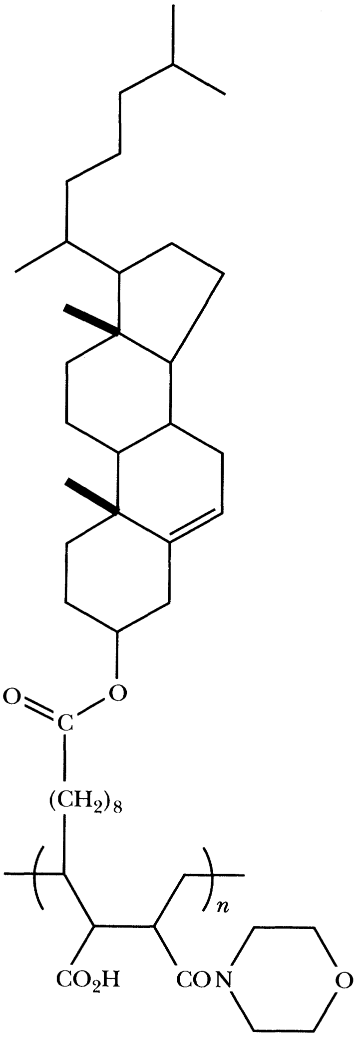


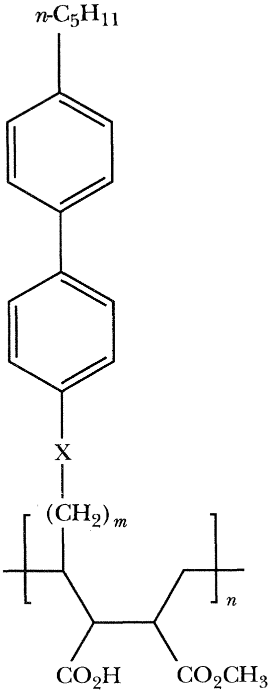
**13**



**14**

## Crosslinking of polymeric Langmuir–Blodgett films

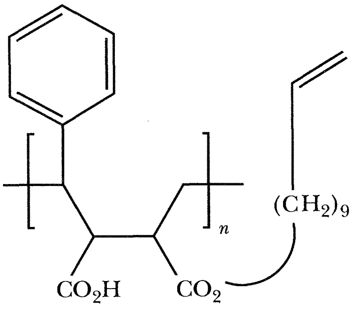
A feature of LB films of particular interest with respect to applications in molecular electronics and optoelectronics is the ability to draw patterns in the films, for example, circuits or wave guides, in a similar manner to the technology used in silicon chip manufacture. Just as ω-tricosenoic acid **2** can be polymerized using an electron beam, LB films prepared on silicon from polymers containing appropriately placed vinyl groups can be crosslinked. Thus, multilayers of the polymer **18** can be crosslinked, presumably at the lipophilic–lipophilic interface (see figure 6), on exposure to an electron beam. Crosslinking greatly reduces the solubility of the polymer and the system has been developed to serve as an electron beam resist with submicrometre resolution (Jones *et al.* 1987). LB films of the same polymer **18** can be crosslinked by UV irradiation, though the limit to the resolution obtainable has not been determined. Similarly, LB multilayers of polymers **19** and **20** can be crosslinked at the



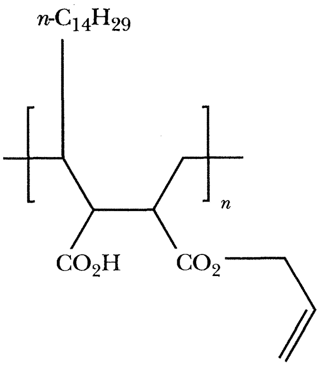
**15** X = $CH_2$ ; $m = 9$

**16** X = CO; $m = 8$

**17** X = CO ; $m = 2$



**18**



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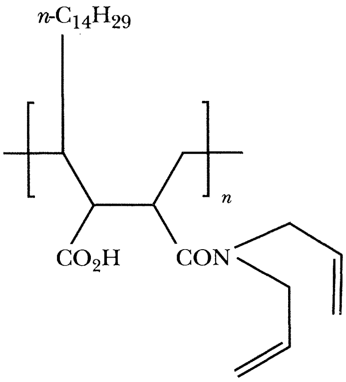


**20**

hydrophilic–hydrophilic interface by using UV-irradiation. Interestingly, X-ray studies show that this leads to a significant reduction in the bilayer spacing (Davis & Hodge 1990).

It should be noted that because crosslinking the multilayers made from preformed polymers increases their stability and renders them insoluble, this paves the way for carrying out organic reactions on LB films.

## POSSIBLE APPLICATIONS

Because polymeric LB films are more stable and robust than films prepared from low-molecular-mass compounds, they are more likely to be suitable for applications in micro-, molecular- and opto-electronics. If necessary the polymeric films can be further stabilized by crosslinking. Possible applications include the following which are being, or have been, studied by the Lancaster group.

### (*a*) *Photo-resists and electron-beam resists*

Because LB films are very thin they have the potential to serve as very high resolution resists. The use of polymer **18** as an electron-beam resist with submicrometre resolution has already been noted (Jones *et al.* 1987). Doubtless, polymers **19** and **20**, or their styrene analogues, could also be used as resists. However, resist technology using spun polymers layers now leads to a much higher level of resolution than is likely to be required in the electronics industry for some years to come. Until the present technology limits progress, there will be no significant commercial demand for LB film resists.

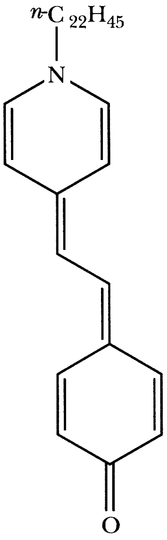
### (*b*) *Sensors*

Many sensor devices involve recognition species bound to electrodes. LB films are very attractive for such applications because they are so thin. Chemical sensor species could probably be bound by the chemical modification of crosslinked, and therefore stable and insoluble, polymeric LB films. Biosensor molecules such as enzymes could be bound similarly without affecting the organized layer structure of the film. Alternatively, because most enzymes or other biosensors are far larger than the species they detect, they could perhaps be physically trapped in between polymeric films crosslinked on the water surface. The polymer will then serve, in effect, as an insoluble semipermeable membrane of molecular dimensions.

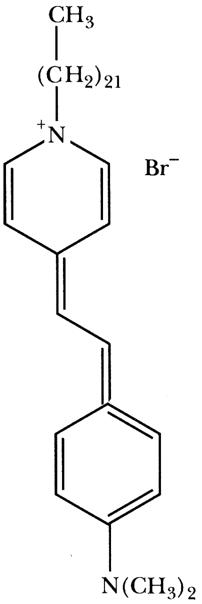
### (*c*) *Nonlinear optical devices*

There has been a great deal of speculation about the use of the LB technique to fabricate optical waveguides having nonlinear properties. Most of the work published has dealt with systems containing only a few layers of material whereas any practical device requires multilayer structures having a thickness of the order of 0.5 μm. Most thick LB layers formed from low-molecular-mass species have light-scattering properties that correspond to an attenuation of hundreds of decibels per centimetre and they are, therefore, unlikely to be useful for optical devices. However, several of the preformed polymers discussed above lead to LB films with relatively low attenuation. By very careful control of cleanliness and biological contamination, optical waveguides several hundred layers thick and having an attenuation of *ca.* 11 dB $\mathrm{cm}^{-1}$ have been produced from polymer **17** (Tredgold *et al.* 1987).

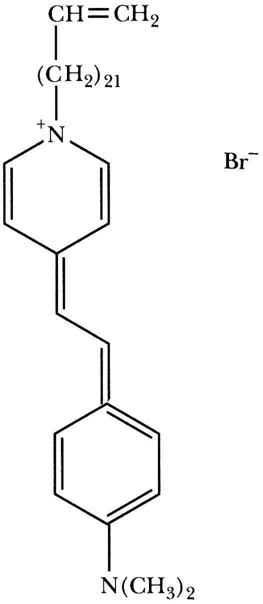
Second harmonic generation (SHG) requires the preparation of films which contain polarizable chromophores such as merocyanine **21** or hemicyanine **22** but which contain no centre of symmetry. This can in principle be achieved by preparing alternating LB multilayers of appropriate materials. The preparation of LB alternating multilayers from two different polymers has so far proved difficult. However, good multilayers can be prepared from one polymer and one non-polymeric material and these multilayers appear to be quite stable. An



**21**



**22**



**23**

LB multilayer was therefore prepared by using polymer **17** and merocyanine **21**. This multilayer gave good SHG but an atmosphere of ammonia was needed to stabilize the merocyanine **21** (Tredgold *et al.* 1988). Analogous films using polymer **17** and hemicyanine **22** are under investigation. To further stabilize the system it may be possible to bind hemicyanine **23** into the alternating films by crosslinking.

## CONCLUSIONS

LB multilayers can be prepared from various preformed polymers. Low-angle X-ray scattering indicates that they contain regular layer structures. These multilayers are more stable and robust than LB films prepared from low-molecular-mass compounds and are therefore more suitable for device application.

Preparation of LB alternating multilayers from two different polymers is difficult, but alternating multilayers from a low-molecular-mass compound and a polymer have been prepared without difficulty. This may prove to be the easiest way of preparing stabilized functional films.

Polymers with appropriately located vinyl groups can be crosslinked by UV light or an electron beam. This not only stabilizes the multilayers, it also allows patterns to be drawn in the films. This could be useful for the preparation of circuits or waveguides.

There are various areas where polymeric LB films might find application in the fields of sensors and optoelectronics.

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## *Discussion*

J. Silver (*Department of Chemistry and Biological Chemistry, University of Essex, U.K.*). Can the formed crosslinked LB films be heated to open the crosslinks? And are strain effects in the layers obtained as they shrink when they crosslink?

P. Hodge. I do not think that heat would break the crosslinks. There is no evidence for strain in the layers. However, as noted in the paper the bilayer spacing decreases on crosslinking.

H. J. Coles (*Liquid Crystal Group, Physics Department, The University, Manchester, U.K.*). Polymer films formed by Langmuir–Blodgett films tend to be polycrystalline so that light propagating along the film experiences a relatively high level of scattering. This poses problems in the generation of nonlinear optical signals because phase matching and polarization of the pump light are not likely to be maintained. One solution to the problem is to use incident light perpendicular or nearly so to the plane of the LB film. Because films of 50–100 layers are typically used the phase-matching problem is overcome as is the scattering effect if suitably small laser beam diameters are used. The problem this poses is that the poled donor–acceptor groups have to lie essentially in the plane of the LB film (i.e. in the direction of polarization of the incident light). In *Y*-type films using suitably tilted functional groups this criterion might well be met. Has Professor Hodge prepared such films and if so how good was the performance of the materials in comparison with the systems with functional groups perpendicular to the substrate?

P. Hodge. We have not studied the attenuation of light passing perpendicularly through the films. However, LB films prepared from preformed polymers do not craze and are not polycrystalline. The attenuation of light in the plane of such films is much lower than with low-molecular-mass compounds.