

Stabilisation of smectic thin films by ultraviolet radiation

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Multilayers of a particular biphenyl compound change from a crystalline to an untilted smectic phase at 54 °C and can be stabilised in this phase by UV irradiation producing a homeotropic phase at room temperature.

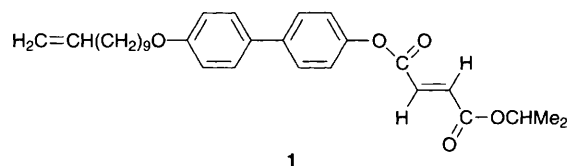
We have synthesised compound **1** by methods which will be described elsewhere and its structure has been confirmed by NMR and IR spectroscopy and its purity confirmed by elemental analysis. This compound can be deposited both by the Langmuir–Blodgett (LB) technique and by thermal evaporation *in vacuo* (TE) so as to form ordered thin films consisting of a multilayer structure having a bilayer repeat unit. Films formed by the TE method were 100 nm thick and LB films consisted of 50 bilayers. We have studied this compound by DSC, by microscopic techniques of the type traditional in liquid-crystal studies¹ and as ordered thin films. In all three cases there is a crystal to smectic B transition at *ca.* 54 °C and, in the case of bulk material, there is another transition from smectic B to smectic A at *ca.* 99 °C. In all three cases there is a transition to the isotropic phase at *ca.* 103 °C. We have studied thin ordered films of this compound both by polarising microscopy and by low-angle X-ray diffraction. Below 54 °C we observe a two-dimensional polycrystalline structure but above this temperature we observe a homeotropic phase. On cooling there is a delay time of the order of 12 h before the crystalline structure reappears. In both the crystalline and the homeotropic phases there is clear X-ray evidence for the existence of a regular layer structure parallel to the substrate. The exact *d*-spacing of the structure depends initially on the method of preparation as will be discussed below.

We have exposed freshly cooled LB multilayers and TE multilayers of this compound to unfiltered light from a mercury lamp for typical periods of 12 min in a nitrogen atmosphere. Films so treated remain indefinitely in the homeotropic phase but it is clear from X-ray studies that a regular layer structure still persists. As we have already pointed out, films not subjected to the UV treatment relax to a polycrystalline structure over a period of about 12 h. We have also studied a compound **2** similar to **1** but without the double bond in the tail unit. In the case of this material there is only one crystal to smectic transition as evidenced by DSC studies. There is, moreover, a striking difference between the behaviour of these two materials. Unlike **1**, **2** returns to the crystalline state immediately on cooling. Furthermore we have attempted to influence the behaviour of this compound by irradiating it with UV light while maintaining it at 60 °C. In this case the irradiation appears to have no effect. Thus the presence of the double bond in the tail is critical for the interesting phenomenon which we have observed. We have examined UV absorption spectra of films of these compounds both before and

immediately after heating. For compound **1** it is possible to observe a significant reduction in the peaks centred at *ca.* 214 and 254 nm immediately after heating. The former peak is associated with the fumarate group and the latter with the biphenyl group. We thus conclude that, in the case of the homeotropic phase, the axis of the biphenyl group lies approximately normal to the plane of the film. X-Ray diffraction data reported below indicate a significant increase of the *d*-spacing when the crystalline to smectic transition takes place as would be expected if this transition is accompanied by a reduction in the tilt of the molecules.

We have examined the effect of the method of deposition on the structure of the films. Compound **1** deposited by TE^{2–4} onto a glass substrate held at –10 °C showed some evidence for the formation of three-dimensional crystals. However, films deposited by thermal evaporation onto either glass or quartz microscope slides at 25 °C consisted initially of the homeotropic phase but, after storage for 12 h, took on regular two-dimensional crystalline structure. We obtained similar good regular crystalline films when we used the LB technique (here the newly formed films consisted of two-dimensional crystals) employing the following deposition conditions. Deposition took place at a surface pressure of 24 mN m^{–1} on slides (rendered hydrophobic by treatment with hexamethyldisilazane) using a dipping speed of 4 mm min^{–1} and a waiting time between strokes of 3 min. The subphase was doubly distilled deionised water. The deposition ratio on the upstroke was 1.1 but never better than 0.3 on the downstroke. It is likely that rearrangement took place immediately after deposition to form a Y structure, a phenomenon observed with many LB materials. Films formed by TE and studied by low-angle X-ray diffraction consisted initially of two phases having slightly different *d*-spacings. After heating to 60 °C and cooling to room temperature and storing for 12 h we obtained films which produced similar diffractograms to those obtained from films formed by the Langmuir–Blodgett technique [Fig. 1(a)]. These results correspond to a repeat distance of 2.9 nm but there is some evidence for the existence of a bilayer repeating structure (a Y structure in Langmuir–Blodgett terminology). Fig. 1(b) corresponds to a multilayer which has been heated to 60 °C, cooled to room temperature and immediately afterwards irradiated with UV light. In this case the predominant repeat distance is 3.2 nm. This result supports our belief that, in the homeotropic phase, there is little or no molecular tilt.

The presence of the double bond in the tail unit is clearly critical for the interesting phenomenon which we have observed. In an effort to understand its function we have formed a film of **1** approximately 1 μm thick, heated it to 60 °C and afterwards irradiated it with UV light at room temperature. This film was exposed to THF in a Soxhlet apparatus for 70 h. The resultant solution was examined by GPC using polystyrene standards. We found a peak in the molecular mass distribution corresponding to a polymer having an average of 84 repeat units. We then re-examined the film by X-ray diffraction. The higher-order peaks had disappeared but the first peak remained though it had been broadened. We have also used UV spectroscopy to confirm that a considerable proportion of the multilayer survives treatment with THF in the Soxhlet



apparatus. We conclude that the material had been polymerised and partially cross-linked by exposure to UV light. We have formed films on quartz slides and studied their UV absorption

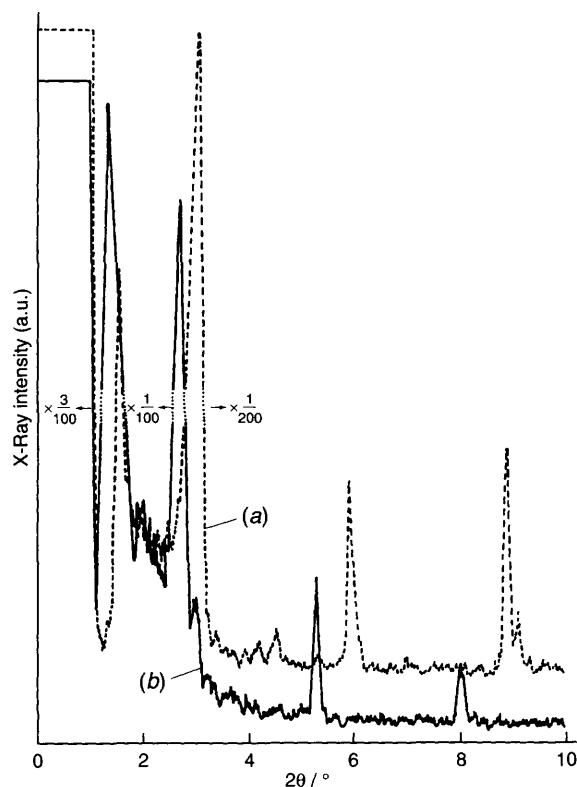


Fig. 1 X-Ray diffractograms obtained from a 100 nm thick film of **1** using Cu-K α radiation having a wavelength of 0.154 nm. (a) Polycrystalline form, (b) homeotropic form.

spectra both before and after irradiation by intense UV light. The reduction of the peak corresponding to the fumarate group brought about by irradiation by UV was slight which is surprising in view of the large degree of polymerisation which appears to have taken place. This result suggests that it is the double bonds in the tail units which polymerise rather than the fumarate groups. On the other hand, related materials without the fumarate group which we have studied and will report on elsewhere do not polymerise readily under the influence of UV. We thus incline to the view that both the fumarate groups and the terminal double bonds take part in the polymerisation process.

We believe that this stabilisation of a homeotropic structure, if it could be extended to other materials, would be of considerable importance. One of the major difficulties in applying the Langmuir-Blodgett technique has been the tendency for many of the materials deposited by this method to organise themselves into a two-dimensional polycrystalline structure. This factor has made it impossible, for example, to form good optical waveguides by the LB technique except when preformed polymers are used.⁵

We are now in the process of studying other related compounds which behave in a similar manner to **1**.

References

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