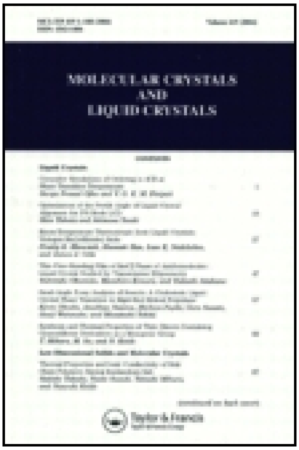

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In-Plane Anisotropy and Phase Change in Langmuir-Blodgett Films of a Triphenylene Derivative

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IN-PLANE ANISOTROPY AND PHASE CHANGE IN LANGMUIR-BLODGETT FILMS OF A TRIPHENYLENE DERIVATIVE

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ABSTRACT

The "in-plane anisotropy" of a triphenylene derivative in Langmuir-Blodgett (L.B.) films has been investigated. Upon heating, L.B.films exhibit a reversible phase transition appearing as an abrupt increase from a low to a high "in-plane anisotropy" corresponding to the formation of the same hexagonal liquid crystal phase observed in the bulk material at almost the same temperature, with the columnar axis aligned along the dipping direction.

INTRODUCTION

In the present work, we have studied the "in-plane anisotropy"(I.P.A.) versus temperature in LB films of an hexasubstituted triphenylene derivative ,which is known for its discotic mesomorphism(1) and its ability to form stable monolayers(2,3). The molecular structures of this compounds is given in figure 1 and correspond to a disk shape. In the bulk material, a phase change towards a columnar phase D_{ho} occurs at 44°C and the isotropic melt at 77°C.

The L.B.films of this compound have been studied through the compression isotherm and Brewster Angle Microscopy. After transfer, Infra Red Linear Dichroism (IRLD) method together with low angle and transmission X-ray experiments allow one to evaluate the IPA of these films, in relation with the temperature of the samples.

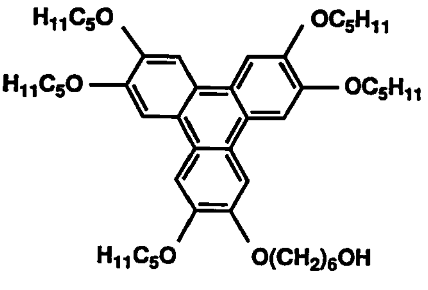

Fig1: The triphenylene derivative used in the present work .

EXPERIMENTAL

Details on the L B method and Brewster Angle Microscopy are given elswhere (4).For infrared linear dichroism measurements, films are deposited onto IR transparent slides ($30\times10\times2$ mm^3 optically polished calcium fluoride or silicon wafers 0.5 mm thick). The spectra are recorded at normal incidence for the light electric vector parallel (//) and perpendicular ($\perp$) to the dipping direction . The degree of anisotropy is characterized by the dichroic ratio R_σ defined as:$R_\sigma = A_\sigma(\perp) / A_\sigma(//)$ where A_σ is the absorption coefficient for the wave number σ. For low angle X-ray experiments, films are deposited onto any rigid and optically polished substrate (calcium fluoride slide or "thick" silicon wafer).For transmission X-ray experiments, films are deposited onto an ultrathin optically polished silicon wafer (typical dimensions: $10\times5\times0.01$ mm^3). The extremely low absorbance of the substrate for the radiation of copper (λ = 1.542 Å) allows to work both in the transmission and reflection geometries. Measurements are performed with a three-circles goniometer mounted on a rotating anode generator (microfocus, 55 kV, 20 mA). This apparatus is equipped with a home-made linear detector and is also suited for taking photographs. The beam was kept perpendicular to the dipping direction and crossed the sample for an arbitrary value of the incident angle θ defined as the angle between the beam and the normal to the substrate ($-90° \leq \theta \leq 90°$). The sample was surrounded by a small temperature controlled home-made oven (inserted into the vacuum vessel of the X-ray apparatus). Recording X-ray photographs requires an exposure time of five to ten hours (when recording an IR spectrum requires only a few minutes). The instability of the samples in vacuum and beyond 50°C restricts a study based only on photographs. In the present work, we have studied the thermal behavior of films using an X-ray detector because it requires only a few minutes for the exposure time and we have focused, as it can be seen below, our attention on the 14 Å equatorial reflection.

RESULTS

The main results are the following:

1) Transfer efficiency ca 0.8 decreasing as the number of deposited monolayers increases (rigid film).

2) Molecular area 52 Å^2/molecule at the transfer pressure of 22 mN/m.

3) Optically clear varnished aspect and interplanar distance of ca 18 Å.

Heating the samples up to 46°C does not lead to any modification of the room temperature initial IPA.(fig 2) ,but heating the films at 50°C results in a very abrupt and huge increase of the dichroic ratio for all the IR lines as shown in fig.4 When cooling back the sample down to room temperature, the high temperature phase is slowly reversible (ca 24h) and the initial IPA is restored. Beyond ca 80°C, an isotropical phase is irreversibly obtained. Besides, a striking feature is to be found in a close inspection of spectra . Whereas for as grown films at room temperature (fig 2) four IR lines are either moderately polarized (1438, 1174, 1056 cm^{-1}) or even not polarized at all (1617 cm^{-1}), in the high temperature phase (T> 50°C ,fig.4) those lines acquire nearly the same IPA as that of the other four (the set of R values lie in between 3.67 and 5)

Anticipating the conclusion derived in the course of the present paper at this step such a behavior is understood in terms of a major change not only in the IPA of the molecular aggregation but also in the intrinsic nature of the molecular aggregation itself. i.e. a phase change. In fact, this seems to be, at our knowledge, the first reported reversible phase transition from a low to a high in-plane order state in an LB film.

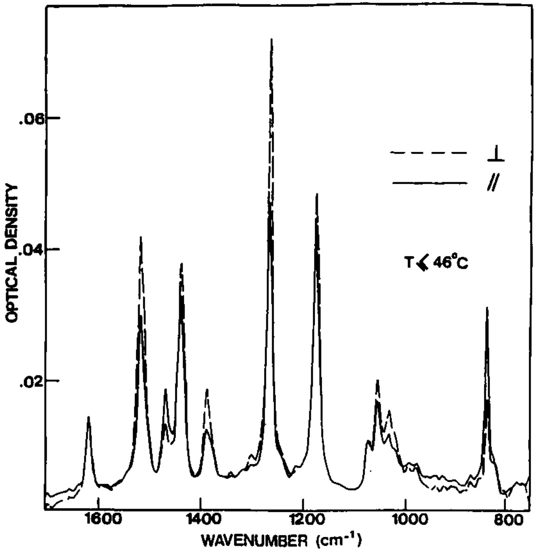

Fig.2: IRLD spectra recorded in the crystalline phase (T≤ 46°C). Full line: electric light vector parallel to the dipping direction. Dotted line: electric light vector perpendicular to the dipping direction. Twenty superimposed monolayers on each side of a silicon substrate made hydrophobic by dimethyl dichlorosilane treatment.

In order to have more details about this new phase, we have devoted a special effort to the transmission X-rays experiments performed on LB films.

DISCUSSION

1) Organization in the Langmuir-Blodgett films

Several arguments lead to the conclusion that in as grown films the aromatic cores stand on edge perpendicular to the substrate.The first one comes from the molecular area extrapolated to zero pressure (i.e.: 67, Å^2/molecule) wich is quite consistent with an "edge-on" organization. Such a model is also supported by the low compressibility of films expected for a condensed phase in which the aromatic cores stand on edge in a direct face to face interaction. In fact, this hypothesis is also supported by the IR data. In the range 1000-1500 cm^{-1}, all the lines are found to be unpolarized or preferentially polarized perpendicular to the dipping direction (fig.2). A precise assignment of those lines is not available. However, we have to consider that among the squelettal motions of the benzene rings, all those polarized "in-plane" of the aromatic cores fall in that particular energy range. In contrast, the 837 cm^{-1} one is clearly polarized parallel to the dipping direction and should be assigned to some squelettal vibration polarized out of the plane of the aromatic cores. All these arguments are again consistent with a configuration in which aromatic cores stand "on edge" with their planes approximately perpendicular to the dipping direction.

The most convincing indication of this "edge-on" configuration in these LB films comes yet from X-ray experiments. X-ray photographs (cf fig 3) were taken for samples at normal incidence (θ=0°), the dipping direction set vertical. Several crescent-like sharp reflections are visible, indicating a high degree of crystallinity. No determination of the unit cell has been tried yet. However, the following features can be pointed out:

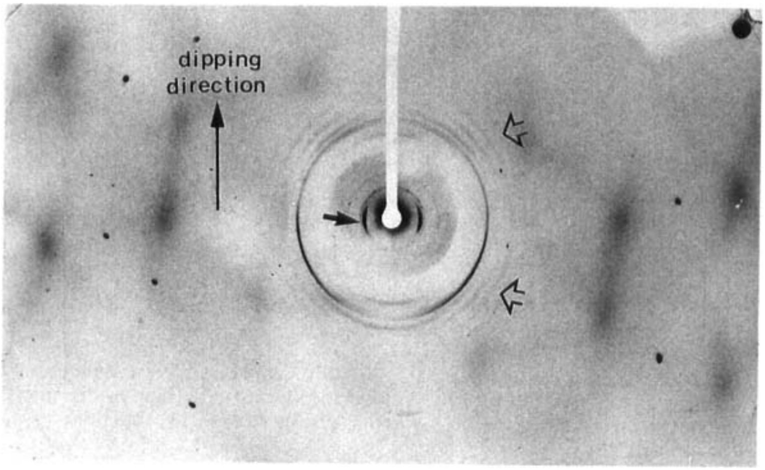

Fig3: Transmission X-ray diagram. The black arrow denotes the d = 14Å reflection and the open arrow the ± 4.84Å one. Fifty superimposed monolayers on silicon wafer 10 micron thick precoated by five underlayers of behenic acid.

1) Two intense reflections at d = 14 Å can be seen on the equatorial (horizontal) line (black arrow in the figure). Such spacing is reasonably close to intercolumnar one (i.e., 16.4Å) found in the bulk material for a D_{ho} mesophase of a closely related compound (reference 2 p 666). Furthermore, the lateral extension of the reflection lines is an additional proof of the molecular in-plane orientation.

2) Several arrays of reflections are found at a distance ± 4.84 Å from the equator (open arrows).and the product 4.84 x 14 = 68 Å^2 is in a reasonable agreement with the molecular area deduced from the

π-A diagram and appears as a direct proof on an "edge-on" configuration. Finally, tilting the sample around the dipping direction gives the stacking periodicity, i.e., the interplanar distance. Five orders of reflection are visible and lead to a value of interplanar distance 18.11 Å. Such a value compares also well with the intercolumnar distance found in the above LC mesophase. All these distances are in agreement with a molecular model in which the molecules stand on edge in columnar aggregates with their short chains interpenetrated (4).

2) Initial IPA

The origin of the initial IPA is not well understood. However, the Brewster Angle Microscopy (BAM) allows one to bring out some comments.

Before any compression,the monolayer of has a striking and clear organization at the gas-water interface. Indeed, , it is made up of "short sticks" which are small birefringent domains (about 400x40 μm^2 at 25°C). Those domains seem to acquire some orientation during the compression process, with their long axis more or less parallel to the compression direction (4). For surface pressure higher than 5 mN/m, those seem to coalesce to give a uniform monolayer. Such a behavior is in a good agreement with a high degree of crystallinity evidenced by X-ray measurements in built up films. It could also explain the finding of a transfer efficiency lower than unity and decreasing as the number of superimposed monolayers increases. Very large "rigid" crystalline domains are not favorable at all to a correct control of the surface pressure around the sample and may be responsible of a poor transfer efficiency.

Even if the monolayer appears homogeneous at high surface pressure, these molecular sticks could still be present in the film. This particular organization together with the already exposed theory(5) of flow orientation induced by the dipping process could explain the initial IPA recorded for transferred films .

3) Thermal behaviour.

The dramatic change in the IPA of films observed by IRLD when heating the sample (fig. 4)is also recorded for the same temperature using transmission X-ray experiments. The intensity of the d = 14 Å reflection was measured versus temperature. Setting the sample at normal incidence (θ=0°), this intensity remains almost constant up to 46°C and decreases to zero at 50°C. However, after each intensity measurement at θ=0°, the sample was rotated by 30° and the scattered intensity recorded. Under these conditions, a sharp reflection appears above 50°C. Such a result should be considered as a clear cut proof of the appearance of a hexagonal columnar phase with the columnar axis preferentially aligned along the dipping direction. So far, the thermal instability of the sample prevent more precise investigation of the hexagonal phase. However, the intercolumnar distance remain close to 14 Å. From the above result, it can be concluded that this phase is basically the same hexagonal D_{ho} phase as that occurring in the bulk material between 44 and 77°C. Coming back to IRLD experiments, a close examination of fig.4 (compared to fig. 2) reveals a general abrupt broadening of the IR lines, ca 30%, (without any detectable shift unless for the 1174 cm^{-1} one). Such a finding is retained beyond 80°C in the melt "isotropic" phase and confirms some liquid behavior for a molecular organization in which, in the mean time, the aromatic cores remain highly oriented. In contrast, together with almost the same general above broadening, the dichroic ratio of the 1460 cm^{-1} weak line jump from 0.55 to a value close to unity (0.94). As that particular line is clearly assigned to the H-C-H scissoring mode of the aliphatic substituents, one may also conclude that the side short external chains are melt in the LC phase.

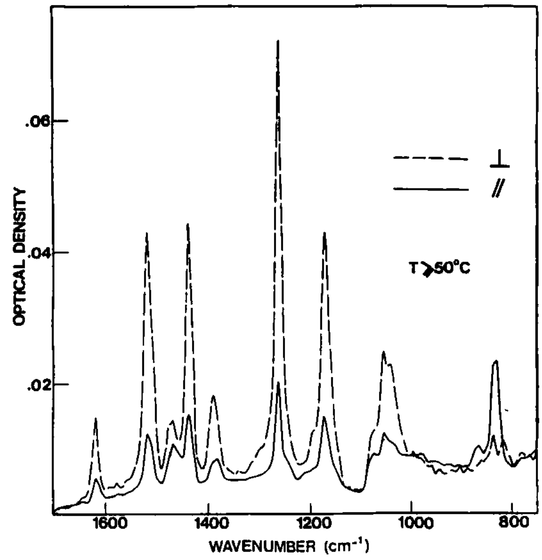

Fig.4 IRLD spectra recorded in the hexagonal D_{ho} LC phase at T ≥ 50°C. Full line: electric light vector parallel to the dipping direction. Dotted line: light electric light vector perpendicular to the dipping direction.

One can summarize the results obtained with LB films of as follows:

1) LB films undergo the same phase change at almost the same temperature as those of the bulk material.

2) This change induces an abrupt increase of the IPA at ca 50°C.

This abrupt increase in IPA when heating films may be a consequence of the initial structure of films which are, as written above, highly crystalline ones and do not contain much free volumes. The initial molecular anisotropy is weak and the average angle between the normal to the aromatic cores and the dipping direction is ca 35 degrees. Retaining the same IPA in the hexagonal phase would mean that the columnar axis actually make the same average angle with the dipping direction. Considering that the columns behave as long and rigid rod like entities, such a mechanism would create a large amount of free volumes and internal stress in the film. In fact, the observed thermal behavior is likely nothing but a simultaneous building of columns and annealing of the induced free volumes (and/or internal stress) leading to a molecular array in which the columns are parallel to each other.

Explaining the reversibility of the phenomenon when cooling back the sample requires an additional assumption. When the film is heated between 50 and ca. 75°C, the low temperature anisotropic structure of the first (or of the few firsts) layer may be retained because of the interactions with the substrate. Therefore, cooling the sample would be nothing but a usual epitaxial mechanism with the first layer as template, inducing a polycrystalline structure with an average IPA close to the initial one.

CONCLUSION

The in-plane orientation observed for as grown films is presumably to be related to a flow orientation during the film compression and transfer. When heated at 50°C, films undergo an abrupt phase change appearing as a strong increase of the IPA. This is clearly connected to the formation of a columnar hexagonal phase to be likely the same as that observed in the liquid crystqlline bulk material. Such a striking behavior is understood in terms of formation of columnar hexagonal array in the film and simultaneously annealing of free volumesand(or) internal stress during the phase change.

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