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Research News

Monolayers and Langmuir-Blodgett Multilayers of Discotic Liquid Crystals?

By André Laschewsky *

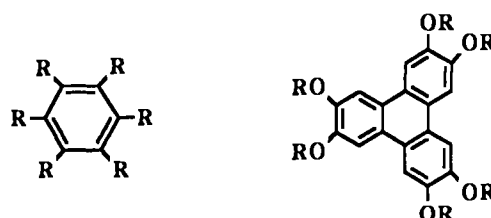
1. Discotic Liquid Crystals

Discotic liquid crystals^[1] were discovered in 1977. They are formed by disk-shaped molecules, i.e. typically by large planar aromatic, or by rather inflexible macrocyclic moieties, surrounded by a number of flexible so-called "wing groups". A selection of discotic liquid crystals (LCs) is shown in Figure 1.

Discotic LCs exhibit columnar mesophases which distinguish them from the well-known calamitic (rod-shaped) LCs. These columnar phases are characterized by stacks of the disk-shaped cores, packed in various ways.^[1]

2. Monolayers and Langmuir-Blodgett Multilayers

Ordered monomolecular layers are formed by the self-organization of water-insoluble amphiphilic molecules at the gas-water interface.^[3] The standard amphiphiles used for monolayers have a polar head group and one or two hydrophobic chains, e.g. fatty acids or phosphatidylcholines respectively. Under appropriate conditions, the monolayers of many amphiphiles can be transferred successively onto solid substrates, by dipping the substrate vertically or horizontally

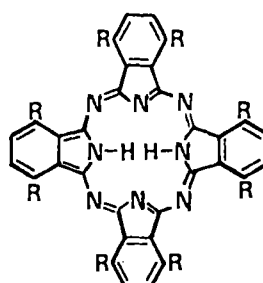


1: R = OOC-C₇H₁₅

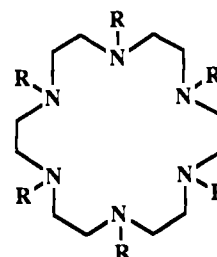
3: R = C₅H₁₁

2: R = C≡C-C₆H₁₃

4: R = OC-C₇H₁₅



5: R = C₈H₁₇



6: R = CO-CH=CH-C₆H₄-OC₁₄H₂₉

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Fig. 1. A selection of discotic liquid crystals [2, 9, 10].

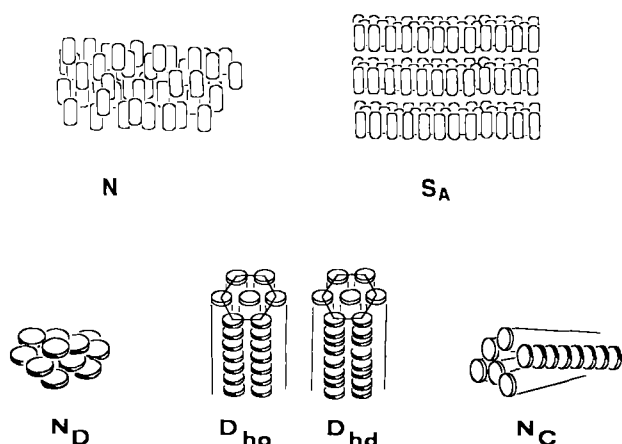


Fig. 2. Scheme of some mesophases: calamitic (rod-shaped) LCs: N = nematic, S_A = smectic A; discotic (disk-shaped) LCs: N_D = nematic discotic, N_C = nematic columnar, D_{ho} = discotic hexagonal ordered, D_{hd} = discotic hexagonal disordered.

through the monolayer.^[3, 4] If the ordered monolayer structure is retained during the transfer process, these so-called Langmuir-Blodgett (LB) multilayers are characterized by molecularly defined thickness, defined anisotropic arrangement of the amphiphiles within the layers, and defined surface structure (Fig. 3). Therefore these ultrathin organic

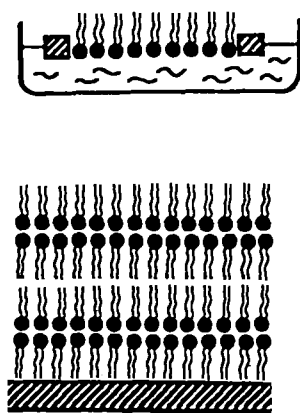


Fig. 3. Scheme of monolayers and Langmuir-Blodgett multilayers.

films are valuable systems for scientific studies, and many potential technical applications have been proposed.^[4, 5]

The formation of monolayers is not restricted to standard amphiphiles. In principle any combination of the number of head groups and of hydrophobic chains is possible. Thus with hydrocarbon wing groups and polar cores, many discotic LCs meet the criteria of amphiphiles, even if they appear to be rather exotic. In fact, in the search for functionalized monolayers and multilayers, many rigid disk-shaped molecules have been investigated since the 1930s, in particular porphyrins and phthalocyanines.^[3-5]

3. Theoretical Considerations on the Molecular Packing of Discotic LCs in Monolayers and Multilayers

The major interest in monolayers and LB-multilayers of discotic LCs derives from their "exotic" molecular shape. It is speculated as to whether this shape can modify the self-organization at the air-water interface to produce thin films of new structure. Perhaps, with a combination of liquid crystalline behavior and amphiphilic self-organization this can be achieved, as proposed in the concept of "amphotropic systems".^[6] These ideas are illustrated in Figures 4 and 5.

When spread on the water surface, discotic LCs can orient in two extreme arrangements called "side on" and "edges on". With the wing groups acting as hydrophobic chains, four types of arrangements of the discotic LCs must be considered which are referred to as types A, B, C and D.

Through the deposition of the monolayers, four types of LB-multilayers of different structure can be produced, corresponding to the monolayer arrangements A-D.

Type A arrangement preserves the conformation of the discotic LCs in the bulk columnar phase, reduced to two-dimensions. Deposition of such monolayers, with the discotic cores of subsequent layers in register, would lead to columnar LC phases with molecularly defined heights of the columns^[7] (Figs. 4a, 5a).

Type B arrangement (Figs. 4b, 5b) corresponds to classical amphiphilic behavior, as the disk-shaped core represents the polar part of the molecule. In this case, the conformation deviates considerably from the one in the bulk LC phase. The amphiphilic character is dominant. Deposition of type B monolayers produces the sandwich bilayer structure of classical LB multilayers, i.e. a structure similar to the smectic mesophases of rod-shaped LCs. Hence in bulk, unknown smectic phases of discotic LCs may be obtained via self-organization due to their amphiphilic character.

The "edge on" arrangements C and D imply that intermolecular interactions between the disk-shaped cores take place. In the special case of type C, strong interactions are required as some hydrophobic wing groups have unfavorably close contact with the water (Figs. 4c, 5c). That is, the discotic LC character of the molecules dominates the amphiphilic character. Such strong interactions may cause the

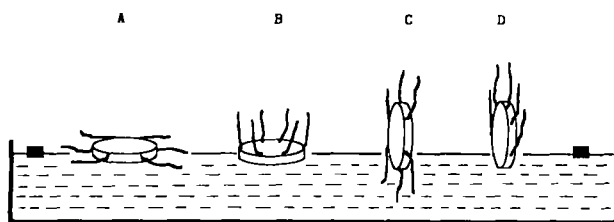


Fig. 4. Possible arrangements of discotic LCs at the gas-water interface: A = side on, chains random, B = side on, chains oriented, C = edge on, chains random, D = edge on, chains oriented.

discotic cores to form stacks, as seen for columnar mesophases (Fig. 2). If such "floating columns" are aligned in the monolayer, two-dimensional nematic columnar mesophases could be formed. If, however, such columns are deposited in register to LB-multilayers, thin columnar phases are produced where the columnar long axis is parallel to the surface of the support (Fig. 5c).

Type D arrangement (Figs. 4d, 5d) represents the compromise between self-organization due both to the amphiphilic and the discotic character. At the same time the interaction of the hydrophobic wing groups with water is small, whereas the interaction between the disk-shaped cores is fairly strong. As discussed for type C, type D arrangement would enable the formation of "floating columns" of the disks, with the possibility of two-dimensional nematic mesophases. Deposition of type D monolayers would create a novel hybrid structure of simultaneous columnar and smectic character (Fig. 5d).

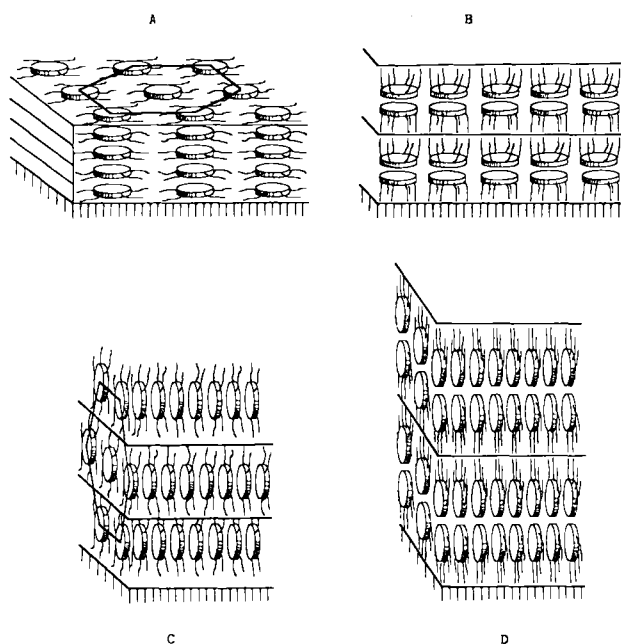


Fig. 5. Hypothetical structures of Langmuir-Blodgett multilayers obtained from discotic liquid crystals: A = side on, chains random, B = side on, chains oriented, C = edge on, chains random, D = edge on, chains oriented.

The monolayer and multilayer structures presented in Figs. 4 and 5 are only hypothetical, representing the "ideal cases". Intermediate or less ordered arrangements are possible, and three-dimensional aggregation may successfully compete with monolayer formation. Nevertheless, the possibility of designing such ordered structures of molecular dimensions is intriguing.

In addition to the unique structural combinations of liquid crystalline and amphiphilic structures, multilayers of many discotic LCs will be useful from the classical point of view as well. They could provide the particular properties expected

from large non-liquid crystalline disk-shaped amphiphiles, e.g. improved thermal stability and conductivity or photoconductivity.^[4, 5] In fact, the presence of the wing groups around the disk core in the discotic LCs will be an advantage in improving the solubility in the spreading solvents and probably decreasing the tendency to form microcrystallites at the gas-water interface.

4. Spreading Experiments with Discotic LCs

Up to now there have been only a few reports on spreading experiments with discotic LCs.^[7-10, 17] Unfortunately, much of the experimental data available is ambiguous and therefore the conclusions drawn may be disputable. In general, surface pressure vs. area diagrams alone are not sufficient to determine the monolayer structure. Additional analysis, e.g. by ellipsometry, fluorescence microscopy, polarized UV/Vis/IR-spectroscopy, X-ray scattering or electron diffraction is required. Comparisons with the more plentiful investigations on non-liquid crystalline amphiphiles with disk-shaped moieties, e.g. porphyrins^[11] and phthalocyanines, may prove to be helpful, but many of those results are also controversial.

Despite all shortcomings in monolayer experiments and their discussion, the present data suggest that extended hydrocarbon wing groups and strongly polar groups favor the "side on" arrangement of the disks, i.e. classical amphiphilic behavior, as observed for compound 6.^[10, 17] In contrast, weakly polar groups and rather short wing groups apparently favor "edge on" arrangements.^[8] However, if the wing groups get too short, and the interaction of the disks too strong, three-dimensional crystallization may occur, as found for compound 2.^[12] In fact, the preferred arrangement of a discotic LC seems to depend on a subtle balance in the molecular architecture. The spreading behavior of the triphenylenes 2 and 3 may serve as such an example.^[8] Thus, appropriate molecular design may allow us to control the type of self-organization in the monolayers.

5. LB-Multilayers of Discotic LCs

Reports on LB-multilayers of discotic LCs^[8-9, 12] are even rarer than monolayer studies. As many of the monolayers are very stiff, deposition by the LB-technique can be difficult to achieve.^[9] Successful transfer has been reported for triphenylenes 3 and 4.^[8] The presence of Bragg diffraction peaks in the X-ray data of the deposited LB-films (rarely observed in multilayers of disk-shaped amphiphiles) demonstrates an ordered layered structure, exemplifying the usefulness of discotic LCs for LB-multilayers. Their detailed structure is not yet clear, although the X-ray data of these triphenylene multilayers points to different types of arrangement of the discs such as type B for 4 and C for 3.^[8]

Interestingly, optical in-plane anisotropy has been observed in LB-multilayers of some phthalocyanines,^[13, 14] supporting a two-dimensional nematoid arrangement of columnar stacks (implying types C or D). However, such in-plane anisotropies have recently been reported for the monolayers and multilayers of many amphiphiles,^[5] and thus seem not to be unique for disk-shaped amphiphiles. The explanation of the in-plane anisotropy is still controversial.

6. Polymeric Discotic LCs

Because of the scarcity of data on low molecular weight discotic LCs, it is difficult to predict how polymeric discotic LCs will behave. The spreading behavior of classical polymeric amphiphiles is more complicated than that of their corresponding monomers,^[3, 6] and this will also be true for the spreading behavior of monomeric and polymeric discotic LCs. If monolayer formation is still possible, a stabilization of the "edge on" arrangement of the disks may be expected. In particular, stack formation could be enhanced using a central polymer backbone.^[15] However, with little data available,^[12] it seems premature to discuss in depth the spreading of polymeric discotic LCs.

An alternative way to tailor "edge on" arranged monolayers may be the formation of charge-transfer complexes. The enhanced formation of molecular stacks and columnar mesophases by charge-transfer complexation has recently been shown in bulk discotic LCs,^[16] and perhaps this method can be transferred to monolayers of discotic LCs.

7. Summary

The field of monolayer and multilayer films of discotic LCs is at its very beginning. The scope and limitations of this preparation method have not yet been explored, and little is known about the structures obtainable. However, the poten-

tial access to extraordinary, ordered thin films is fascinating, and will stimulate research in the future.

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