Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Polymorphism in Langmuir Films from a Fluorescently Marked Phospholipid

George R. Ivanov [a] & Alexander G. Petrov [a]

[a] Laboratory of Liquid Crystals and Molecular Electronics, Institute of Solid State Physics, Bulgarian Academy of Sciences, Blvd. Lenin 72, 1784, Sofia, Bulgaria

Version of record first published: 24 Sep 2006.

To cite this article: George R. Ivanov & Alexander G. Petrov (1992): Polymorphism in Langmuir Films from a Fluorescently Marked Phospholipid, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 215:1, 245-252

To link to this article: http://dx.doi.org/10.1080/10587259208038531

Mol. Cryst. Liq. Cryst. 1992, Vol. 215, pp. 245–252
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

POLYMORPHISM IN LANGMUIR FILMS FROM A FLUORESCENTLY MARKED PHOSPHOLIPID

GEORGE R. IVANOV AND ALEXANDER G. PETROV
Laboratory of Liquid Crystals and Molecular Electronics, Institute of Solid State Physics, Bulgarian Academy of Sciences, Blvd. Lenin 72, 1784 Sofia, Bulgaria

(*Received March 11, 1991*)

Abstract Surface pressure - mean molecular area isotherm is measured for a monolayer from dimyristoil-nitrobenzoxadiazol-phosphatidylethanolamine at the air-water interface. The observed very rich polymorphism is discussed.

Keywords: langmuir films, fluorescent lipids, P-A isotherms, surface polymorphism

INTRODUCTION

Two-dimensional layers of amphiphilic molecules with polar "head" groups and hydrocarbon "tails" attached to a water/air interface represent a class of physical systems of great interest. Such monolayers bridge the gap between two-dimensional and three-dimensional systems especially in the area of cooperative phenomena and phase transitions. The monolayer polymorphism is of practical interest since it provides a possibility for the controlled preparation of Langmuir-Blodgett (LB) films with heterogeneous lateral organization. In the field of molecular biology monolayers of phospholipids have gained great attention as model systems of biological membranes. Intensive investigations of phospholipids in the last decade by the groups of E. Sackmann[1], H. McConnell[2], H. Mohwald[3] has made this compounds almost as model system for the two chain amphiphilic molecules.

A very valuable technique for the investigation of the shape of domains during phase transitions[4], the nature of the phase transition[5], the defect structure of the crystalline phases[1], the pattern preservation during deposition[6], is fluorescence microscopy. First developed for examination of monolayers on solid supports and at the air-water interface recently the technique was applied for

real-time observation of the LB transfer by monitoring the meniscus area[7]. In most of this investigations of phospholipids as a fluorescent probe DM-NBD-PE (dimyristoil-nitrobenzoxadiazol-phosphatidylethanolamine) was used. Because of its poorer solubility in the condensed phase high contrast microscopic observation is possible. The polymorphism of this substance by itself is, however, largely unknown. It is important to consider this polymorphism, especially at room temperature where most of the above mentioned experiments were carried, for better understanding of the achieved results.

This zwitterionic compound with strong dipole moment is interesting also as a head modified molecule in molecular electronics applications. Commercially available are also tail modified molecules with the same chromophore group and different tail lengths. Systematic investigations of charge transfer and aggregation would be desirable.

MATERIALS AND METHODS

DM-NBD-PE (Fig. 1) (Avanti Polar Lipids, Inc., USA) with purity in excess of 99% was in chlorophorm solution. It was further diluted with chlorophorm (p.a.) to a concentration of 0.1 mg/ml. A new ampule

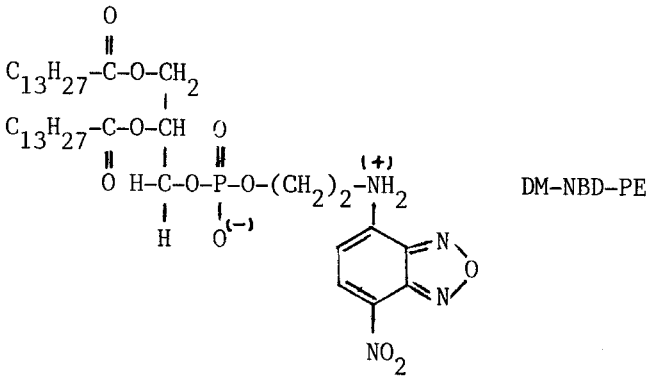

FIGURE 1 The compound used is dimyristoil-nitrobenzoxadiazol-phosphatidylethanolamine

was opened the day the isotherms were taken. Thus effects from oxidation and concentration uncertainties were minimized.

The shape of the isotherm was very critical to cleanliness and the compression velocity. The trough was machined from one piece of bulk Teflon (PTFE) and thus contaminations from seals were avoided. Distilled water with no additives (pH 5.8) was used as subphase. The isotherms were taken on the fully computerized film deposition system designed by us[8]. It comprises Wilhelmy type surface pressure transducer with resolution of 0.02 mN/m, nonlinearity below 1% and long-term drift stability of $\pm$ 1.2 mN/m. Before taking the isotherms a precise calibration of the pressure was performed according to the well known 25.6 mN/m break point of the Arachidic acid. The absolute error of the mean molecular area measurement was below 10^{-9} nm^2 per molecule which is several orders of magnitude better precision than in other troughs. 6 data points were measured per second giving a total of around 8000 data points per isotherm. All measurements were performed at room temperature of 23°C. Compression was started 10 min. after spreading of the monolayer. At compression rate of 0.002 nm^2/(s x molecule) already no kinetic effects were observed and lower speeds did not change the shape of the isotherms. This velocity corresponds to an area decrease of 0.08 cm^2/s. Total trough area is 400 cm^2. When compressibility modulus was calculated a linear least squares curve fit on 80 sequential data points was performed.

RESULTS

The isotherm of DM-NBD-PE together with its compressibility modulus is presented on Figure 2 and the coordinates of some specific points together with a proposed explanation is given in the Table 1.

Several peculiarities should be pointed out. The transitions at points d and e are very sharp and the straight line between them is almost horizontal as judged from the compressibility modulus which is almost zero for that region. This means that in that region a "weak" first order phase transition probably takes place.

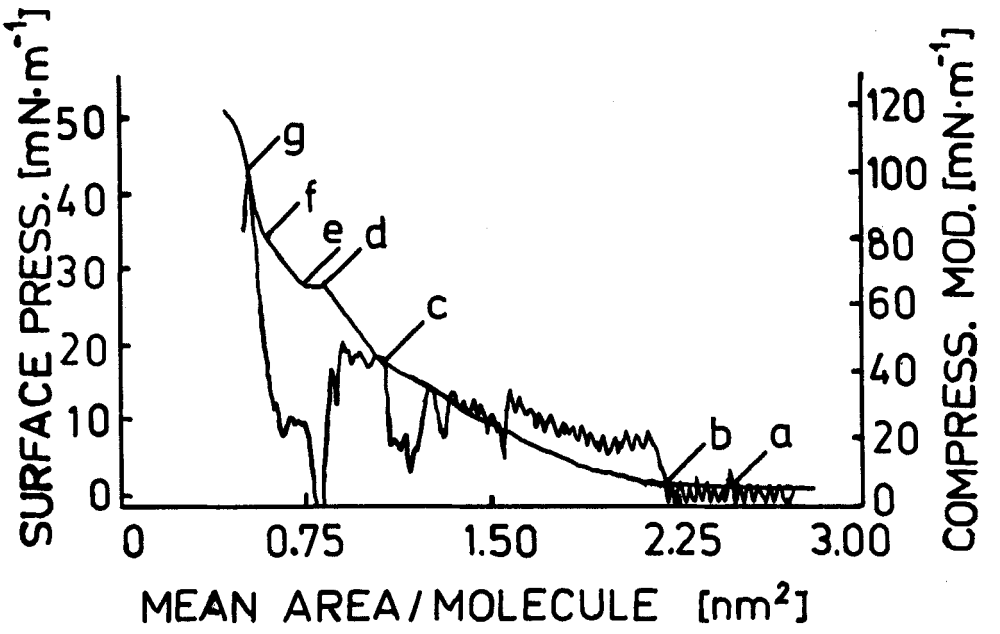

FIGURE 2 Surface pressure vs. mean area per molecule isotherm of DM-NBD-PE at 23°C and its compressibility modulus (the noisy curve).

TABLE I Some characteristic points of the isotherm of DM-NBD-PE at 23°

	P (mN/m)	A (nm^2)	Interpretation
a	0.2	ca. 2.6	beginning of gas to fluid transition
b	0.9	2.23	end of gas to fluid transition
c	16	1.10	isotropic fluid - anisotropic fluid
d	27.5	0.75	beginning of fluid - solid transition
e	27.8	0.68	end of fluid - solid transition
f	34	0.52	solid I - solid II transition
g	ca. 43	0.45	collapse

DISCUSSION

In the literature there are very few discussions of the details of such complex isotherms. It is important however to compare results with similar compounds. The closest to DM-NBD-PE is dimyristoyl-phosphatidylcholine (DMPC) which is also an uncharged zwitterionic phospholipid with bulkier head in comparison to phosphatidylethanolamines. The isotherm is presented on Fig. 3 where also the isotherm of dipalmitoyl-phosphatidylcholine (DPPC) is given.

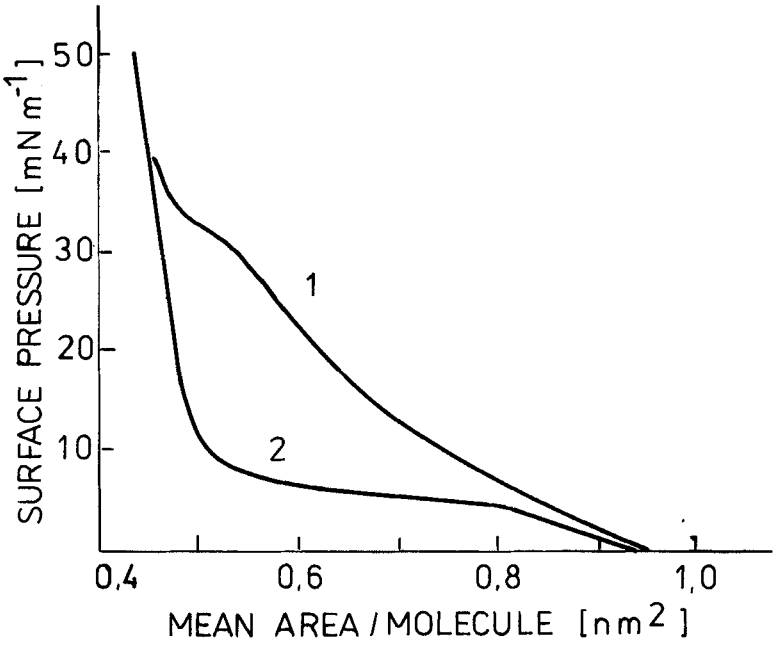

FIGURE 3 Isotherms of dimyristoyl-phosphatidylcholine (1) at 19°C and dipalmitoyl-phosphatidylcholine (2) at 20°C

In the case of DM-NBD-PE the surface pressure rises at more than two times larger mean molecular area. This could be due to the bulkier head and stronger interactions with water because of the higher head polarity. On careful examination of the isotherm an almost horizontal region up to pressures of around 0.9 mN/m is visible where the end of gas to fluid transition is expected. Following the discussion in Ref. 9 a transition from fluid isotropic phase, where there is no orientational order, to fluid anisotropic phase (at

higher pressures) where there is anisotropic orientation of molecules can be ascribed to the point c . This could be a first order phase transition point c being the end of such a transition.

The complexity of interpretation of isotherms of such molecules with large heads comes also from the necessity to describe molecules with at least two stretching vectors describing separately the orientation of tails and heads. Such molecules may also have different crystal lattices in condensed states for the heads and the tails[1].

The beginning of the fluid - solid transition (at point d here) is largely debated in the literature[5]. In the case of DM-NBD-PE the process is probably governed by the head group interactions as seen from the large surface area A = 0.75 nm^2. In contradiction to DMPC and DPPC the decrease in area here is smaller and the end of the "weakly" first order transition at point e is very sharp. At point e the mean molecular area is 0.68 nm^2 which corresponds to the projection of the molecule with fully stretched head in the plane of the water and tails strongly tilted in the direction of the head as calculated from molecular space filling models (not shown). On increasing the pressure probably starts the bending of one of the tails and the head goes partially below the tail projection on a lateral direction. In the region between points e and f bending of the head towards normal direction to the water probably occurs as judged from the relatively large decrease in area. At a pressure P = 39 where A = 0.463 probably the processes are already governed by tail interactions. Two densely packed tails in hexagonal lattice and in all-trans configuration have an area of 0.388 nm^2 [10]. At point f the average tail tilt angle is about 40^o to the normal assuming dense packing and all-trans conformation of the tails as judged from the mean molecular area. Our previous experiments for small-angle X-ray diffraction of LB films from DP-NBD-PE[11] support such a conclusion because they revealed bilayer thickness of 5.21 nm which was shown to correspond to a tilt angle of 40^o. From these measurements the expected thickness for a monolayer from DM-NBD-PE at point f would be 2.35 nm. An increase in the layer thickness of 0.19 nm when increasing the deposition pressure from 35 to 50 mN/m was observed. This is most probably due to tail tilting towards normal direction

ending with an angle of 30° at point g. The conformation of the molecule in this last region is shown on fig. 4. The water level

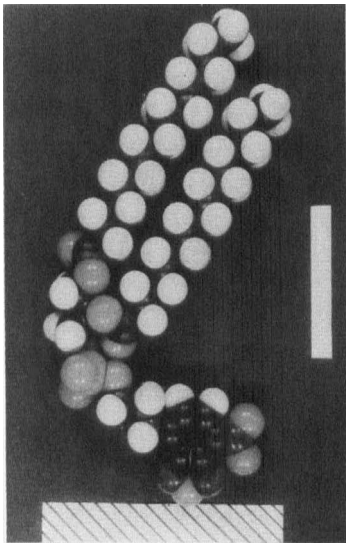

FIGURE 4 Conformation of the molecule of DM-NBD-PE at condensed states. The bar on the right hand is equal to 1 nm.

probably passes through the oxygen atoms of the carboxyl tail groups.

Further experiments like FTIR spectroscopy of LB films are now in progress for better understanding of the polymorphism of DM-NBD-PE.

REFERENCES

1. E. Sackmann, A. Fischer and W. Frey in J. Meunier, D. Langevin and N. Boccara (eds.), Physics of Amphiphilic Layers, Springer Proceedings in Physics, 21, 25 (1987), see the literature therein.
2. M. Seul, P. Eisenberger and H. M. McConnell, Proc. Natl. Acad. Sci. USA, 80, 5795 (1983).
3. H. Mohwald, Thin Solid Films, 159, 1 (1988), see the literature

therein.
4. H. M. McConnell, L. K. Tamm and R. M. Weis, Proc. Natl. Acad. Sci. USA, 81 3249 (1984).
5. A. Fischer, M. Losche, H. Mohwald and E. Sackmann, J. Physique Lett., 45, L-785 (1984).
6. P. Karg, A. G. Petrov, E. Sackmann and A. Wunderlich, J. Molec. Electr., 6, 21 (1990).
7. J. E. Riegler, Rev. Sci. Instrum., 59, 2220 (1988).
8. G. R. Ivanov, A. T. Todorov and A. G. Petrov in P. I. Lazarev (ed.), Molecular Electronics - Materials and Methods, Topics in Molecular Organization and Engineering, 7, Kluwer Academic Publishers, Dordrecht, The Netherlands, (1991); G. R. Ivanov, A. T. Todorov and A. G. Petrov, Proceedings of the III European Conf. on Organized Organic Thin Films, Mainz, Oct. 1990, Macromoleculare Chemie, (in press).
9. O. Albrecht, H. Gruler and E. Sackmann, J. de Physique, 39, 301, (1977).
10. V. Ivkov and G. Berestovsky, Dynamical Structure of the Lipid Bilayer, Nauka, Moscow, chap. 1 and 2, (1981), (in Russian).
11. G. R. Ivanov, submitted.