Phase diagram and collapse of a diacetylenic Langmuir film.

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I. INTRODUCTION.

Amphiphilic monolayers spread at the air-water interface and compressed to beyond the equilibrium spreading pressure of coexistence with the bulk phase (ESP), are metastable and "collapse". Despite considerable effort neither the role of dimensionality and of the range of interactions on molecular ordering nor the mechanisms of collapse have been fully elucidated. The most likely routes to the bulk phase are a slow nucleation and growth process above a pressure $\Pi_{collapse}$ [1] (intermediate trilayer and multilayer states have been observed [2,3]) and, if the compression rate is high, a fracture process at $\Pi_{fracture} > \Pi_{collapse}$. The formation of trilayer structures has been suggested to arise from the buckling and folding of the monolayer [4], although the corresponding energies [5] and wavelengths are probably too large [6]. If a nucleation and growth process is to be retained, the solid bulk phase can either form at defects already present in the monolayer [5], or by homogeneous nucleation [1]. The rate of collapse depends, in particular, on the temperature, the pH [7] and the nature and concentration of the cations in the subphase [8]. The collapse is expected to be strongly dependent on the initial state of the monolayer, and the choice of the solvent as well as the deposition procedure are essential in obtaining reliable results.

10,12 pentacosadiynoic acid (PCA) is a diacetylenic amphiphile that can be polymerized under U.V. irradiation [9]- [11]. Polymerizable diacetylenic films have attracted much attention since the work of Wegner [12] due to their potential applications. In the present context, the PCA presents the advantage of forming at low pressures on water very stable trilayers that can be studied in detail. The film can also be stiffened by polymerization. In this latter case, the much more stable monolayer buckles. All the collapse processes can therefore be studied with this same material.

Collapsed films are highly inhomogeneous. Ignoring this inhomogeneity can lead to serious misinterpretations. In this study we used Brewster angle microscopy (B.A.M.) to image the texture of the films in situ, and atomic force microscopy (A.F.M.) on transferred films when a better resolution was desirable (with the risk of structure or texture change during transfer), together with pressure-area isotherm and x-ray scattering measurements.

II. THE 10-12 PENTACOSADIYNOIC FILM ON A BASIC BUFFER SUBPHASE.

A basic subphase stabilizes the monolayer with respect to tri- or multi-layer growth (see below) [11]. Isotherms of PCA spread on a sodium tetraborate buffer (pH=7.5) at different temperatures ranging between $17^{\circ}C$ and $30^{\circ}C$ are given in fig.1. An expanded phase is formed at a high molecular area. The pressure in the expanded phase starts to increase slowly at about $0.80nm^2/molecule$ to reach a plateau of transition (first order transition) towards a more condensed phase. At a molecular area of about $0.3nm^2/molecule$, the pressure increases again in the condensed phase. Finally the monolayer collapses at a pressure higher than $30mN/m$. X-ray reflectivity experiments have been performed at room temperature in the expanded phase: the overall thickness of the monolayer is $1.76nm$, with $0.70nm$ for the upper alkyl section, $0.26nm$ for the lower alkyl section, $0.4nm$ for the diacetylenic rod, and $0.4nm$ for the headgroup thickness. The expanded phase appears to be rather disordered.

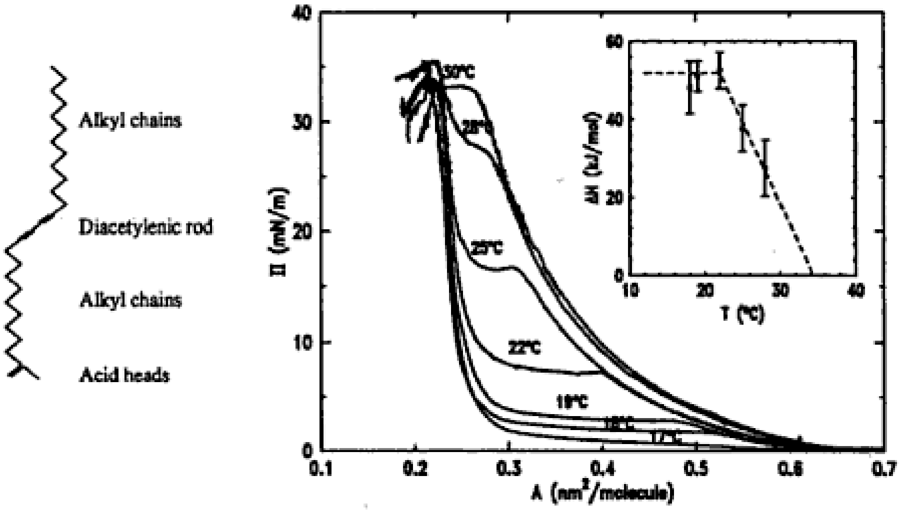

fig.1: *left: schematic of the PCA molecule; right: surface pressure - molecular area isotherms for PCA on a basic buffer and a 1:9 ethanol hexane mixture as spreading solvent at different temperatures Insert: enthalpy of transition.*

The chain thickness in the condensed phase ($2.1nm$) is larger than in the expanded phase. The nucleation and growth of long (up to $600\mu m$), narrow, ramificated domains can be observed by Brewster angle microscopy. Some of the domains appear to grow from a bright nucleus (fig.2 left). By carefully controlling the pH and the temperature, and using the 1:9 ethanol/hexane spreading solvent mixture, a condensed film with very long range order ($1mm$) is systematically observed (fig.2 right). This highly ordered condensed film is ideal for the polymerization.

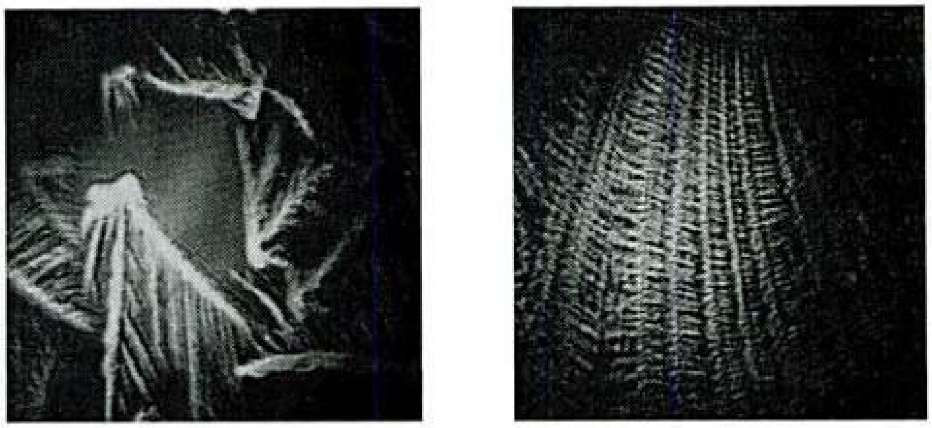

fig.2: *Brewster angle microscopy image on the expanded condensed transition plateau. left: nucleation of domains, right: highly ordered domains at the low area end of the plateau. The image size is* $600\mu m \times 600\mu m$.

III. POLYMERIZATION ON A BASIC BUFFER.

The PCA was exposed to U.V. radiation both in the expanded phase and in the condensed phase. To avoid ozone oxidation (leading to a pressure increase after a few minutes exposure) the polymerization was performed under an Argon atmosphere. In contrast to the expanded phase, a long range polymerization is evidenced in the condensed phase. This suggests that the film has to be condensed and organized enough for polymerization. This is in some way in agreement with the often quoted topochemical nature of the polymerization reaction [9]-[11].

The film area at constant pressure diminishes (about 10%) upon polymerization suggesting a molecular rearrangement, in agreement with the x-ray measurements. The polymerized film can be compressed without collapsing to a much higher pressure than the unpolymerized film ($> 40mN/m$). Grazing incidence x-ray scattering has been performed on a polymerized film compressed to $15mN/m$. A broad peak at $q_x = 4 \times 10^{-4} nm^{-1}$ can be attribuated to the buckling of the film in the third dimension [6] which has been observed with other polymerized systems and should be characteristic of such covalently tethered films without intrinsic tension.

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The χ^2 value can be significantly improved by including a coexistence with a monolayer in the model. Trilayers could also be obtained by deposition of 3-dimensional PCA crystals (no spreading solvent) on water. In the latter case, we do not observe a monolayer, suggesting that the trilayer is the stable phase in equilibrium with the crystal at very low pressure, i.e. the monolayer would always be metastable. A.F.M. images shown in fig.4 obtained respectively at higher and lower pressure than that of the bump, show very different domains. In particular, after the bump (for an area $0.2nm^2/molecule$), the domains are smaller and thicker. This indicates that the collapse occurs at the bump which corresponds to the activation barrier necessary to create multilayer nuclei from the trilayers. Indeed, the smaller size and wide thickness distribution of the multilayer nuclei suggest that their origin is the break or folding of the previously observed trilayers.

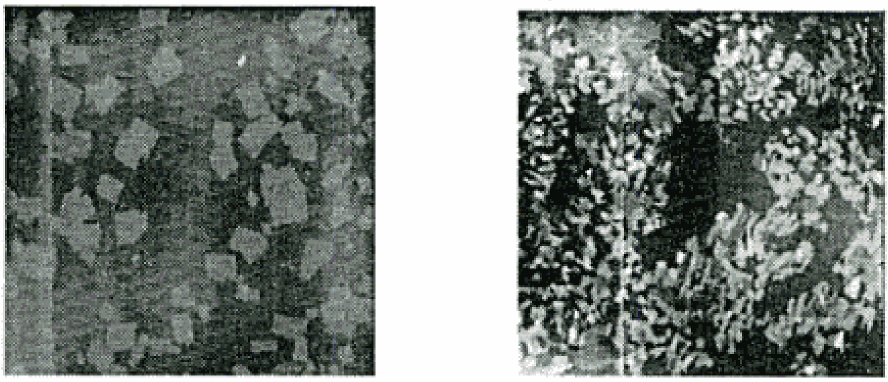

fig.4: *Atomic force microscopy image of the trilayer (left) and the collapsed film (right) deposited on a silicon wafer. The image size is* $100\mu m \times 100\mu m$.

The collapse pressure of PCA is given in fig.3 as a function of the compression velocity. Remarkably, the collapse pressure is linear in the logarithm of the compression velocity:

$$\Pi = \Pi_0 + \theta lnV \qquad (1)$$

with $\theta = (1.63 \pm 0.13)mN/m$. Interestingly, another material forming trilayers at the air-water interface, the liquid crystal 4-cyano-4'-n octylbiphenyl (8CB) does not exhibit any speed dependence of the collapse pressure. 8CB is in a smectic A phase at room temperature. This suggests that in the case of 8CB the trilayer domains can form and/or grow freely whereas the formation and/or growth of "solid" multilayer domains of PCA requires to overcome some additional energy. Briscoe and Evans [13] have studied the sliding friction between two monolayers of fatty acid deposited on molecularly smooth mica substrates using a friction apparatus. They also found $P = P_0 + \alpha lnV$ where P is the pressure applied to the film and $\alpha = 0.42MP$, close to the pressure in the monolayer obtained by dividing

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