

## Liquid Crystalline Texture in Glycine-Modified Diacetylene Langmuir Monolayers at Room Temperature

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Received: September 19, 1994; In Final Form: November 10, 1994<sup>®</sup>

Direct visualization of the self-assembling and liquid crystalline texture formation in glycine-modified diacetylene (Gly-DA) Langmuir monolayers at room temperature is achieved using Brewster angle microscopy (BAM). The striped (smectic) texture appears directly after spreading the monolayer at the air-water interface. The spatial period of this texture has been estimated to be in the range 0.015–0.005 mm, which is in agreement with the range predicted theoretically for this phase. When pressure is applied, the width of the strips decreases and, finally, the striped texture disappears. Another texture appears in the pressure range 30–35 mN/m: the well-defined pseudo-focal-conic texture, which points to a disordered hexagonal columnar mesophase. In addition, direct visualization of the Gly-DA polymerization under UV radiation exposure via BAM is achieved. We observe focal-conic texture reminiscent of smectic C phase.

### Introduction

Recently, the existence of mesophases in Langmuir monolayers of long-chain fatty acids has been firmly established by Overbeck and Möbius<sup>1</sup> via Brewster angle microscopy (BAM) visualization of the detailed texture for these films. These observations have been confirmed by using polarized fluorescence microscopy.<sup>2</sup> The X-ray diffraction study<sup>3</sup> of this newly identified phase transition in fatty acid Langmuir monolayers suggests an explanation of why the transition is not usually seen in the monolayer pressure-area isotherm but is observed in the microscopic texture along a line in the pressure-temperature phase diagram.

In this Letter we report the direct visualization via BAM of mesophase formation in Langmuir monolayers of glycine-modified diacetylene<sup>4</sup> at room temperature. The choice of a new class of the Langmuir monolayers has been prompted by the tendency of the amphiphilic diacetylenes (DA) to self-assemble at the air-water interface.<sup>5</sup> DA can be easily modified by amino acids and, thus, may be used for modeling aspects of living systems, such as biological membranes.<sup>6</sup> The polymerization of DA under the UV light causes the color changes which may be utilized in biomimetic design of biosensors.<sup>6</sup> The biomimetic approach to controlled crystallization (biomineralization)<sup>7</sup> in which the Langmuir monolayers play the role of the two-dimensional organized templates for oriented nucleation requires a detailed knowledge of the monolayer microstructure. Since most processes in living systems occur at room temperature, it is important to study the changes in microstructure specifically at this temperature.

### Experimental Details

Langmuir monolayers were prepared in a Nima round trough (Nima Technology Ltd., Coventry, UK). The mixture of Gly-DA (6.02 mM) in CH<sub>2</sub>Cl<sub>2</sub>/MeOH is first spread over the water surface. About 5 min is then allowed for the solvent to evaporate. Slow compression (80 cm<sup>2</sup>/min) is then applied, and the surface pressure-area isotherm is recorded. The pure water for the subphase was first purified from tap water via reverse osmosis in a Milli-RQ 10 plus unit (Millipore Corp., New Bedford, MA) and then further refined by a Milli-Q plus recycling deionizer-active charcoal filter unit to a specific resistivity of 18.2 MΩ cm.

The diacetylene derivative used was COOHCH<sub>2</sub>NHCO-(CH<sub>2</sub>)<sub>8</sub>C≡CC≡C(CH<sub>2</sub>)<sub>11</sub>CH<sub>3</sub> [*N*-(10,12-pentacosadiynoyl)glycine]. Gly-DA was synthesized by coupling the *N*-hydroxylsuccinamide derivative of polydiacetylene with glycine.<sup>8</sup> For the Gly-DA polymerization under UV radiation exposure, monolayers of the unpolymerized diacetylene were kept in the dark until polymerization was initiated by exposure for a few seconds to 254 nm UV light from a UV lamp source placed at a distance of approximately 2–3 cm from the monolayer.

BAM was invented by Hönig and Möbius in 1991.<sup>9</sup> We used a commercial Brewster angle microscope BAM 1 plus (NFT, Göttingen, Germany). The microscope has been positioned in such a way that the beam points exactly at the center of the Nima trough. Because the visual angle of the BAM camera is about 53° (Brewster angle), the images are compressed in the vertical direction. To correct this, a digital image processing system has been used. The direct visualization of the live microstructure changes achieved with the BAM (resolution about 5 μm) were recorded on a videotape.

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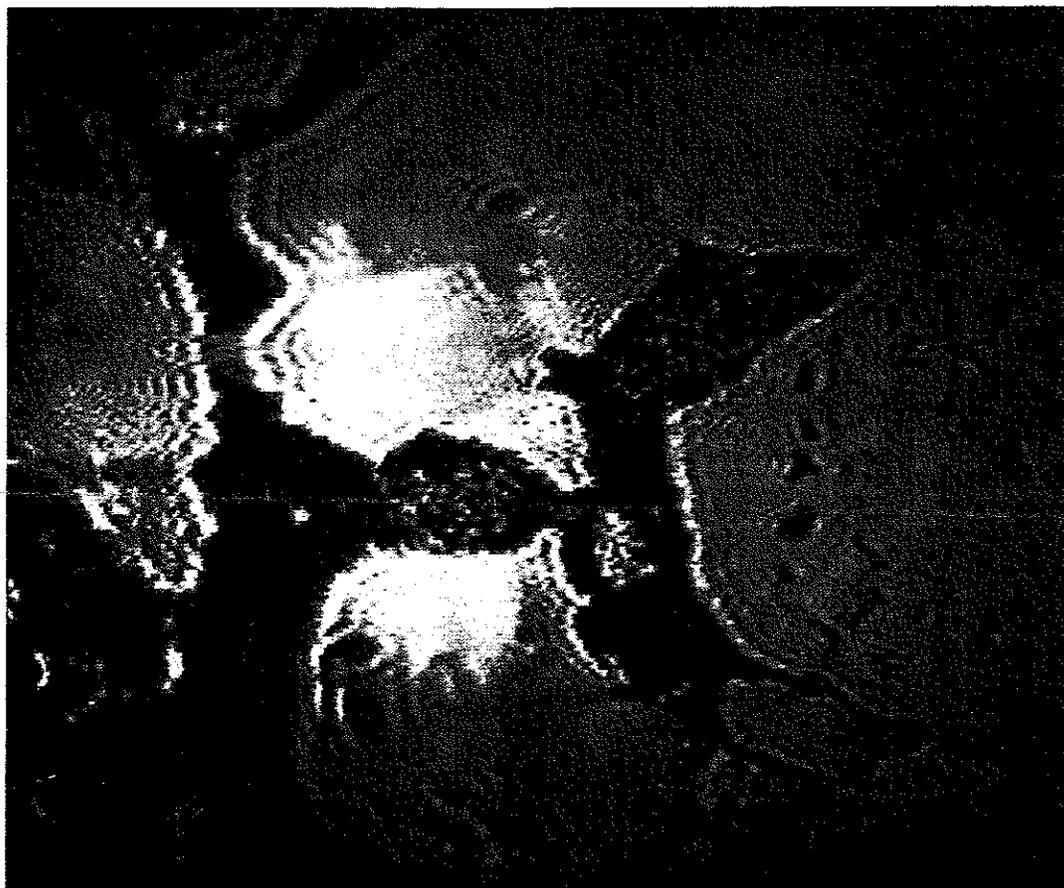
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<sup>®</sup> Abstract published in *Advance ACS Abstracts*, December 15, 1994.

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**Figure 1.** Microscopic texture changes in a Langmuir monolayer of Gly-DA at 21 °C and pressure range 0.5–5 mN/m. The scale of the image is  $1 \times 1 \text{ mm}^2$ .

### Results and Discussion

Figure 1 shows a typical microscopic texture occurring directly after spreading the Gly-DA. At this early stage, self-assembly in the monolayer is recorded, resulting in partial aggregation into more and less dense phases, orientationally ordered and disordered, respectively, called "liquid compressed" (LC) and "liquid expanded" (LE) phases.<sup>10</sup>

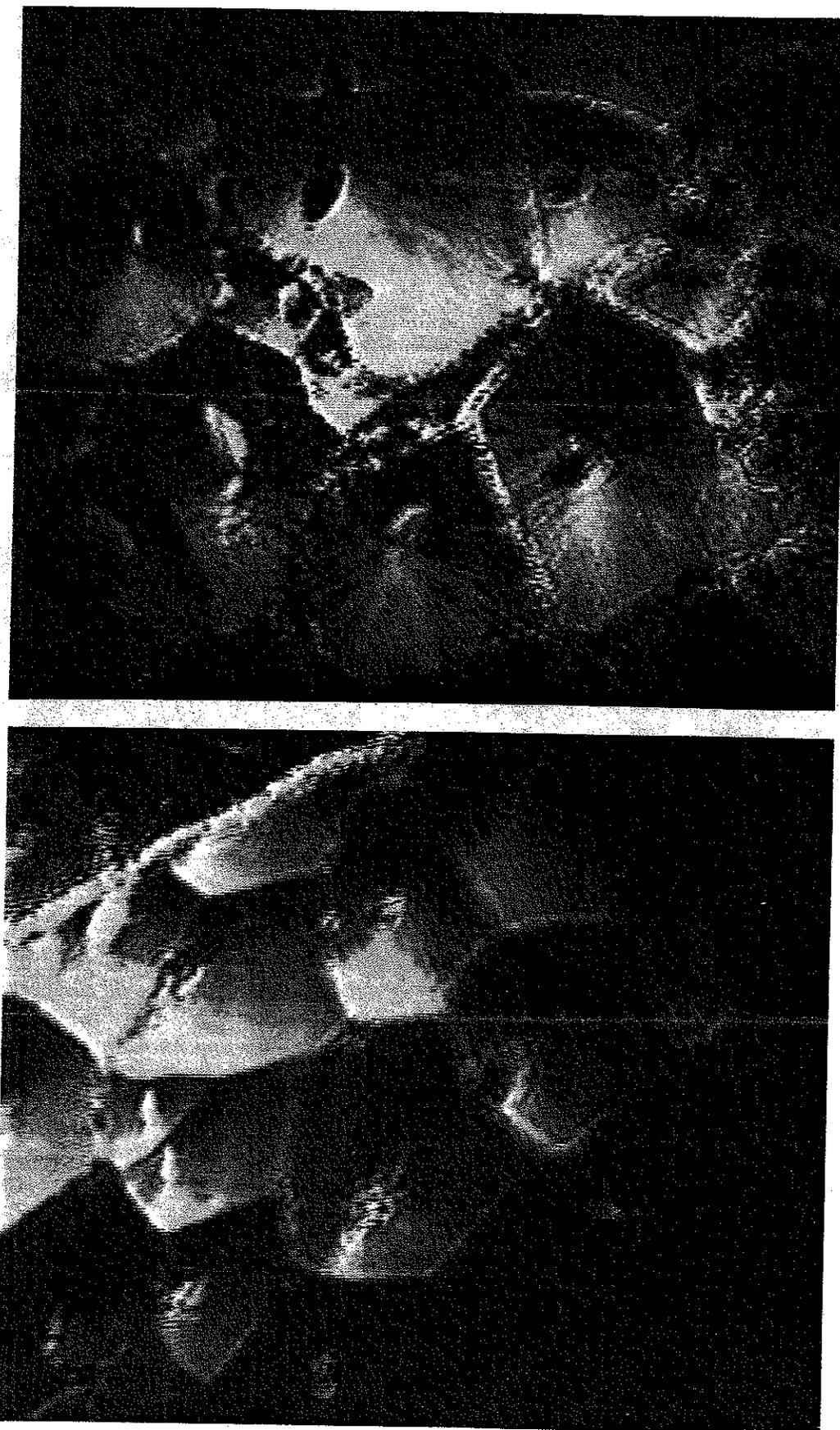
We observe in some regions the undulating structures with stripes of LE and LC domains coexisting and in other regions rather uniform, dense structures forming. In the relatively dense zones of Figure 1 we note the decrease in the width of the stripes. This tendency intensified under further compression then destroys the texture altogether. The average distance between the dark or light stripes of the texture in such a "fingerprint" structure is suggestive of a spatial period for a liquid crystalline structure.<sup>11</sup> Our estimate of this period is in the range 0.015–0.005 mm.

The striped phase observed is qualitatively reminiscent of the one observed by Weis and McConnell in phospholipid monolayers.<sup>12</sup> These findings were theoretically explained<sup>13,14</sup> as the result of competition between long-range attractive dipolar and short-range repulsive van der Waals interactions in the monolayer. In our case, the dipolar interactions are present due to glycine. Thus, it seems appropriate to characterize this newly found phase as a striped (smectic) structure predicted by Andelman *et al.*<sup>14</sup> The theoretical estimate of the undulation period is about 0.01–0.001 mm, which is close to our spatial period estimate.

Figure 2 shows a typical microscopic texture occurring in the pressure range 30–35 mN/m. We observe a well-defined pseudo-focal-conic texture, which points to a disordered hexagonal columnar mesophase ( $D_{hd}$ ).<sup>15</sup> Similar columnar liquid crystalline textures have been observed also at room temperature for pyrazaboles.<sup>16</sup> The only similarity in a chemical structure between pyrazaboles and Gly-DA seems to be a rigid  $\pi$ -system possessed by both the ring in the case of pyrazabole and in our case of two triple carbon bonds. In Figure 2a the domain boundaries are very sharp. In Figure 2b the pressure is close to that of collapse, and the domain boundaries seem much thicker. The boundaries show an interesting structure as the molecules appear to be pushed out of the monolayer.

Figure 3 shows a typical microscopic texture after Gly-DA monomers were converted to the polymeric form by a short exposure to UV radiation. We observe in most regions a "blue" phase with focal-conic texture and the amorphous phase in the rest of the sample. Our findings are qualitatively similar to the study of Batchelder *et al.*<sup>17</sup> in which the model of monolayer growth is proposed via the growth of islands with a high degree of local order and between the islands the molecules are in an amorphous state. We note that the observed texture is reminiscent of smectic C.<sup>18</sup>

Aside from the desire to explore liquid crystalline phases at room temperature, it is also important to characterize the influence of slight changes in physical and chemical properties of the materials used in the reactions. This will help determine the effect of such changes on the ability to form a liquid



**Figure 2.** Microscopic texture changes in a Langmuir monolayer of Gly-DA at 21 °C at  $\sim 30$  mN/m (a, top) and  $\sim 40$  mN/m (b, bottom). The scale of the image is  $1 \times 1$  mm. The analyzer angle is  $80^\circ$ .

crystalline state and will most likely reflect a delicate balance involving characteristics of the structures as well as the

surrounding environment. These types of changes are currently under study.



**Figure 3.** Brewster angle micrograph of Gly-DA polymerized under short UV exposure (254 nm) at 21 °C. The scale of the image is  $1 \times 1 \text{ mm}^2$ . The analyzer angle is  $80^\circ$ .

### Conclusion

We have observed the formation of liquid crystalline texture in Langmuir Gly-DA monolayers via direct visualization using BAM. All of the newly observed phases are not usually reflected in the surface pressure–area isotherm.<sup>13</sup> The striped phase observed directly after spreading appears to coincide with the modulated phase predicted by Andelman *et al.*<sup>14</sup> The pseudo-focal-conic and focal-conic textures have not been observed to date, to the best of our knowledge, for diacetylene based monolayers. Focal-conic texture appears to be stable enough to become very important for future applications as organic templates in oriented nucleation.<sup>7</sup> Our results suggest that BAM may be successfully used, in addition to other monolayer characterization techniques (TEM, Raman, FTIR, AFM), to identify new textures and to specify the monolayer growth mechanisms.

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JP942515G