

# Direct observation by using Brewster angle microscopy of the diacetylene polymerization in mixed Langmuir film

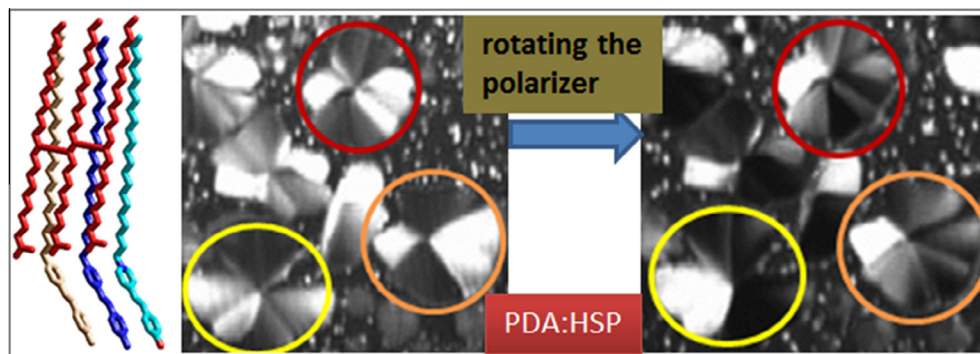


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## GRAPHICAL ABSTRACT



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## ABSTRACT

Mixed Langmuir monolayers of 10,12-Pentacosadiynoic acid (DA) and amphiphilic hemicyanine (HSP) have been fabricated at the air–water interface. The mixed monolayer has been proved to be completely homogeneous. The DA molecules are arranged in a single monolayer within the mixed Langmuir monolayer, as opposed to the typical trilayer architecture for the pure DA film. Brewster angle microscopy has been used to reveal the mesoscopic structure of the mixed Langmuir monolayer. Flower shape domains with internal anisotropy due the ordered alignment of hemicyanine groups have been observed. Given the absorption features of the hemicyanine groups at the wavelength used in the BAM experiments, the enhancement of reflection provoked by the absorption process leads to the observed anisotropy. The ordering of such groups is promoted by their strong self-aggregation tendency. Under UV irradiation at the air–water interface, polydiacetylene (PDA) has been fabricated. In spite a significant increase in the domains reflectivity has been observed owing to the modification in the mentioned enhanced reflection, the texture of the domains remains equal. The PDA polymer chain therefore grows in the same direction in which the HSP molecules are aligned. This study is expected to enrich the understanding and design of fabrication of PDA at interfaces.

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## 1. Introduction

Polydiacetylenes (PDA) can be used as sensor due to their outstanding colorimetric and fluorescence dual detection capability

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[1–3]. Yoon et al. designed a highly efficient colorimetric sensor based on PDA for sensing carbon dioxide, with much noticeable color change [4]. Counterfeit signatures can be stamped on tickets using PDA, being temperature sensing [5,6].

Well-ordered DA monomers either in bulk conditions or at interfaces can be photopolymerized onto PDA by UV irradiation [7–9]. Note that DA polymerization only occurs when the DA monomers are arranged in a highly ordered state, requiring an optimal packing of the DA units to allow propagation of the linear chain polymerization through the ordered phase. The polymeric backbone formed is composed of alternating double and triple bonds, which absorbing light at approximately 650 nm gives a blue appearance [10]. This is the so-called “blue” form of PDA. However, if the effective conjugation length is reduced by the strain and torsion imposed onto the backbone, the absorption maximum is shifted to about 550 nm, and a bright red color is obtained. This latter case is the so-called “red” form of PDA. The backbone rotation can be induced by different stimuli: exposure to heat [11,12], presence of organic solvents [13], pH and salt variations [14], mechanical stress [15], electric current [16,17]. For biosensors this rotation is induced by the specific surface ligand–receptor interaction [18,19]. Previous reports suggest that the release of side-chain strain taking place upon stimulation causes rotation about the C–C bonds in PDA backbone. This conformational change modifies the conjugation degree of the array of p-orbitals, leading to a change in the chromophore group responsible for the electronic transition and ultimately being responsible for the color change that can be observed by naked eye [20]. The process of DA polymerization is therefore quite sensitive to the environmental physicochemical conditions [21].

Concerning the polymerization of DA at air/liquid interfaces, Lifshitz et al. reported on Langmuir monolayers of pentacosadiynoic acid that render the blue and red phases at 0.24 nm<sup>2</sup> and 0.19 nm<sup>2</sup> per molecule, respectively [22]. These results confirm the topochemical control of the DA polymerization, i.e., initial atom positions determine the obtained PDA form [23]. We have described the mixed Langmuir monolayer formed by 10,12-Pentacosadiynoic acid (DA) and an amphiphilic cationic hemicyanine (SP) [24]. Herein, the mixed Langmuir monolayer of DA and the cationic 4-[(4-hydroxy)styryl]-1-docosylpyridinium surfactant (HSP) has been studied. Both the DA:HSP and the DA:SP are homogeneous Langmuir monolayers. The red polymer form is exclusively obtained in both cases. Note that SP and HSP molecules differ only in the terminal dimethylamino group of SP, which is replaced by an OH group in the HSP. Despite this small chemical modification, a significant difference in the behavior of DA:SP and DA:HSP monolayers at the mesoscopic level has been obtained.

Brewster angle microscopy (BAM) has been typically used to monitor the formation and evolution of such mesoscopic domains at the air/water interface occurring in Langmuir monolayers with small surface area, strong hydration, and non-absorption. Indeed, BAM is a powerful technique with a vast range of applications. Fanani et al. elegantly employed BAM for the study of biomolecules at the air/water interface, including ceramides [25–27] and drug derivatives [28]. An alternative focus allowed Caseli et al. to obtain relevant insights in the structure of monolayers concerned with optoelectronic devices [29–32]. Porphyrin derivatives incorporated onto Langmuir monolayers have been also studied by BAM [33–35]. On the other hand, BAM technique has been used by our group focusing in Langmuir monolayers with polar head groups absorbing radiation in the wavelength value of the laser used for acquiring the BAM pictures [36,37]. Note this case of Langmuir monolayers including chromophores observed by BAM is remarkable; given molecules absorb the incoming visible radiation enhance the reflection of such radiation, the observed BAM images of domains are mainly determined by these chromophore

molecules. A theoretical framework for this non-standard usage of BAM is established in a recent review [38]. We basically take advantage of the phenomenon of reflection–absorption. The very same phenomenon is used in other optical techniques for studying the air/liquid interface, for example the IR reflection–absorption spectroscopy (IRRAS) [39,40].

Therefore, BAM has been used to study the DA:HSP monolayer. For the previously studied DA:SP monolayer, small domains without anisotropy were observed, showing elastic properties when the monolayer was decompressed. On the other hand, in the case of the present DA:HSP mixed monolayer, the domains formed larger, showing internal anisotropy, and being rigid. The study of this phenomenon, allows the direct observation on a specific domain, the DA polymerization direction, and whether this direction is parallel at the HSP aggregation axis.

## 2. Experimental section

### 2.1. Materials

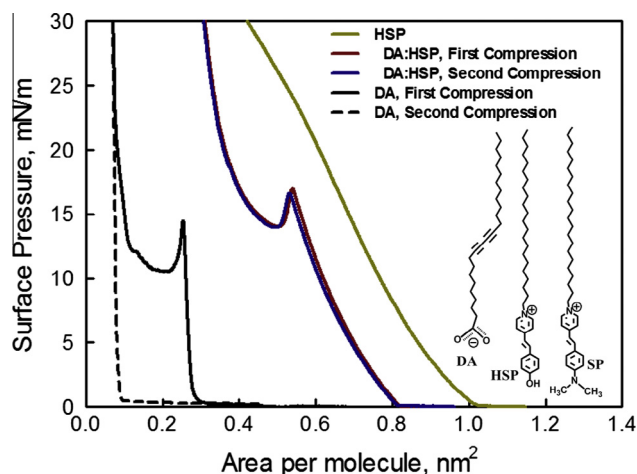
10,12-Pentacosadiynoic acid (DA) was purchased from ABCR (Germany) and purified according to the method described elsewhere [41], that is, the diacetylene monomer was dissolved in chloroform and filtered through a 0.45  $\mu$ m nylon filter. Purified powder was obtained by evaporation of the solvent.

Hemicyanine dye, 4-[(4-hydroxy)styryl]-1-docosylpyridinium bromide (HSP) were purchased from Sigma–Aldrich and used as received. Their molecular structures are depicted inset in Fig. 1.

The initial solutions for each component were prepared as well in chloroform. A mixture of trichloromethane and methanol, ratio 3:1 (v/v) was used as cospreading solvent. The pure solvents were obtained without purification from Aldrich (Germany). Ultrapure water, produced by a Millipore Milli-Q unit, pre-treated by a Millipore reverse osmosis system (>18.2 M $\Omega$  cm), was used as a subphase. The subphase temperature was 21 °C with pH 5.7.

### 2.2. Surface pressure–area isotherms of Langmuir films, reflection spectroscopy and BAM imaging

Two different models of Nima troughs (Nima Technology, Coventry, England) were used in this work, both provided with a



**Fig. 1.** Surface pressure–area ( $\pi$ – $A$ ) isotherms of DA (first compression: black line, and second compression: black dashed line), HSP (green line), and DA:HSP mixed monolayer (first compression: red line, and second compression: blue line). Inset: Molecular structures of DA, HSP and SP from left to right, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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