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Anisotropy in Langmuir monolayers supported by flowing water

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A recently designed Langmuir trough using a steady-laminar flowing subphase is exploited to support polymer monolayers. Atomic-force-microscopy observation of the polymer monolayer deposited on a graphite plate by a horizontal method reveals that the polymer chains are elongated and aligned in the flow direction, which can be understood from a hydrodynamic point of view.

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Many types of polymers and surfactants are spreadable on a water surface to form monomolecular layers known as Langmuir monolayers. Studies on these monolayers have considerably broadened our understanding of the structures and properties of two-dimensional gases, liquids, and various ordered as well as disordered monolayer phases that exist in nature [1–10]. Previous studies on these monolayers have constantly exploited a stationary water subphase, thus the air-water interface is generally regarded as an ideal and isotropic substrate supporting the monolayers [5]. It is conceivable that if other types of subphases, e.g., an anisotropic subphase, are used, the previous observations of the monolayer behavior should be modified to some extent. In this paper we use an anisotropic subphase generated by flowing water for spreading monolayer and study the anisotropy in polymer Langmuir monolayers supported by this anisotropic subphase.

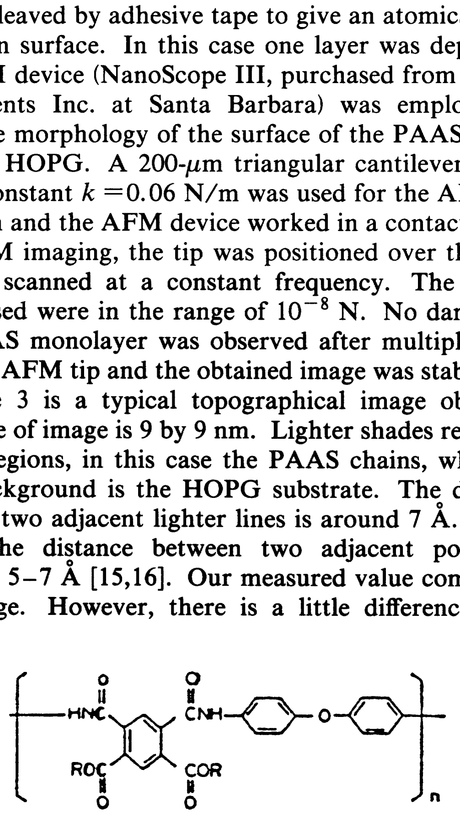
The polymer we used in this study is polyamic acid alkylamine salt (PAAS) obtained by mixing polyamic acid and alkylamine in a molar ratio of 1:2, dissolved in a mixed organic solvent of N,N-dimethylacetamide and benzene (1:1 in a molar ratio). The concentration of the repeated units is 1.0 mM. The average molecular weight of polyamic acid is 4.0×10^4. Figure 1 shows the structure of the PAAS unit. The reason that we choose the PAAS molecules is that the PAAS films are currently used as a precursor of polyimide films, which have found their application in diverse areas such as insulating films [11] and alignment layers for liquid-crystal devices [12].

The Langmuir trough using a flowing subphase was designed by us. The detailed description of the whole system has been reported in [13]. Here, for the benefit of presentation, we give only the schematic diagram of the trough (see Fig. 2). The trough is made of PTFE (Teflon), 165 cm in length, 7.5 cm in width, and 0.5 cm in depth. Double distilled water fills the trough up to the rim of the trough. We have proved that the flowing water is a steady laminar [13].

The PAAS solution (0.1 ml) was dropped onto the flowing water surface at end *A* by use of a microsyringe. A PTFE barrier was placed at end *B* to stop the PAAS monolayer from floating away so that the PAAS molecules can accumulate and be compressed at the left-hand side of the barrier. In the course of our experiment, the flux was controlled at 30 ml/min. The distance between the barrier and the position where monolayer deposition occurs was about 60 cm. All the experiments including the following atomic-force-microscopy (AFM) imaging were operated in air at room temperature (25 °C).

The compressed PAAS monolayer was transferred onto a highly oriented pyrolytic graphite (HOPG) substrate by a horizontal method. The process is similar to that described in Fig. 2 of [14]. The HOPG plate was freshly cleaved by adhesive tape to give an atomically flat and clean surface. In this case one layer was deposited. An AFM device (NanoScope III, purchased from Digital Instruments Inc. at Santa Barbara) was employed to study the morphology of the surface of the PAAS monolayer on HOPG. A 200-μm triangular cantilever whose spring constant $k=0.06$ N/m was used for the AFM observation and the AFM device worked in a contact mode. For AFM imaging, the tip was positioned over the sample and scanned at a constant frequency. The typical forces used were in the range of 10^{-8} N. No damage to the PAAS monolayer was observed after multiple scans with the AFM tip and the obtained image was stable.

Figure 3 is a typical topographical image obtained. The scale of image is 9 by 9 nm. Lighter shades represent higher regions, in this case the PAAS chains, while the dark background is the HOPG substrate. The distance between two adjacent lighter lines is around 7 Å. As we know, the distance between two adjacent polyimide chains is 5–7 Å [15,16]. Our measured value comes into this range. However, there is a little difference. The



$R = NH_3C_{16}H_{33}$

FIG. 1. Structure of polyamic acid alkylamine salt unit.

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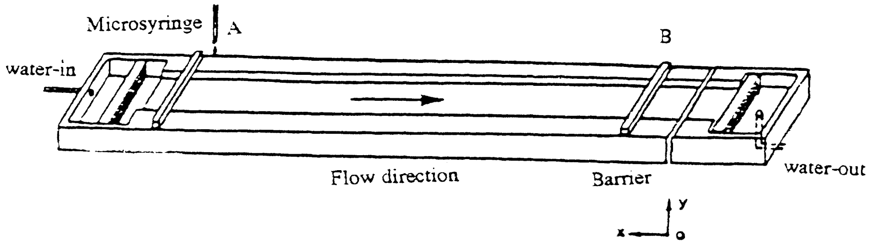

FIG. 2. Schematic diagram of the trough using a flowing subphase. The large arrow indicates the flow direction.

PAAS is the precursor of polyimide. But we think the gaps between parallel molecular chains should not make much difference.

It is worthy to note that in Fig. 3 the PAAS chains are practically parallel to the flow direction. To check the orderedness of polymer chains on a larger scale, we scanned the sample in different regions and found that the polymer chains are almost oriented in the same direction, i.e., the flow direction. The oriented polymer chains in Langmuir-Blodgett films have been addressed previously [14,17–19], wherein the films were prepared by a vertical method. By a horizontal method, however, here we have also observed aligned chains. To understand the alignment mechanism, we analyze this anisotropy from a hydrodynamic point of view.

Suppose the trough is w in width and d in depth. In the following we would not pay attention to the dynamic process when the PAAS monolayer is compressed forward. Instead, we focus on the static behavior of the monolayer. A coordinate system indicated in Fig. 2 is adopted in the analysis. The origin of the x-y system is fixed on the bottom right under the barrier.

According to the theory of hydrodynamics [20], the velocity $v(y)$ of a steady-laminar incompressible viscous flow inside two parallel stationary plates can be expressed as

$$v(y)=[(y^2-yd)/2\mu]\frac{dp}{dx} ,$$

where μ is the viscosity of the fluid and dp/dx is the gradient of the water pressure along the flow direction. Thus, the average velocity of fluid $\bar{v}$ can be written as

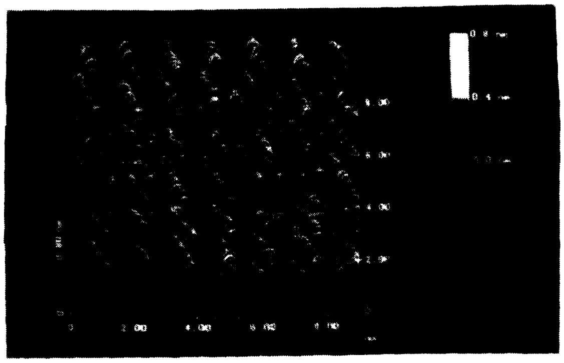

FIG. 3. A 90×90 Å^2 AFM image of the polyamic acid alkylamine salt monolayer deposited on HOPG. The flow direction is from bottom to top.

$$\bar{v}=\int_0^d v(y)dy/d=(-d^2 12\mu)\frac{dp}{dx} , \tag{1}$$

where the negative sign means the direction of flow is opposite to the pressure gradient. Taking Eq. (1) into account, the rate of shear of the fluid, defined as the velocity gradient in the y direction, is

$$\frac{dv}{dy}=[(2y-d)/2\mu]\frac{dp}{dx}=-6\bar{v}(2y-d)/d^2 . \tag{2}$$

Substituting $y=d$ into Eq. (2) gives the rate of shear at the water surface

$$\left.\frac{dv}{dy}\right|_{y=d}=-6\bar{v}/d=6Q/wd^2 ,$$

where Q is the flux. The shear stress acting the monolayer can be expressed as

$$\tau=\mu\left.\frac{dv}{dy}\right|_{y=d}=6\mu Q/wd^2 .$$

And the shear force (per unit length) acting the monolayer can be integrated as

$$\pi=\pi_0+6\mu Q(1-x)/wd^2 , \tag{3}$$

where π_0 is the force acting the monolayer at the position $x=1$. Therefore, the polymer chains in the monolayer subject to a flowing subphase tend to thread in the flow direction due to this shear force. In the monolayer this stress force may be counterbalanced by the force caused by the elongation of polymer chains.

The process arranging the molecular chains in the flow direction is very similar to the rubbing process [21], an ordinary treatment employed in fabricating the alignment layers for liquid-crystal devices. However, the alignment due to a flowing subphase occurs in a two-dimensional space, while the rubbing process is performed in a three-dimensional space. In some sense, rubbing the monolayer by flowing water underneath may be a better and controllable treatment, for example, considering Eq. (3), the rubbing strength can be easily monitored by controlling the flux.

The technological implications of the presented study are clear: The trough can be used to compress as well as align polymer materials, especially, with high surface viscosity. Ordered chains orientation is essential in some situations, e.g., in the production of the high-strength and high-modulus fibers [22] and in the fabrication of alignment layers for liquid-crystal devices [14,15,19]. It is understandable that the reported experiment configuration can also align rodlike molecules. Therefore, the polymerization rates in this system can be pronouncedly increased [23].

In summary, we have employed a recently designed Langmuir trough, in which the subphase flows unidirectionaly, for spreading polymer monolayers. The polymer monolayer deposited on graphite by a horizontal method has been observed by atomic-free-microscopy. We have found that the polymer chains are aligned along the flow direction. The alignment property is understandable from the standpoint of hydrodynamics.

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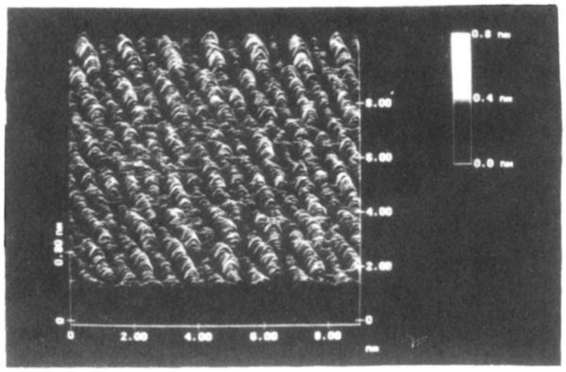

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