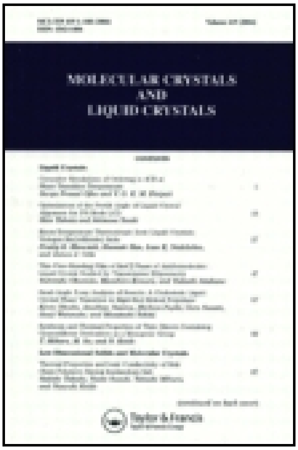

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Liquid Crystal Alignment on Polyimide Langmuir–Blodgett Films

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A vertical dipping method is normally employed to prepare polyimide (PI) Langmuir–Blodgett (LB) films for liquid crystal (LC) alignment due to its dipping effects. In this paper, however, we exploited a horizontal method to make PI LB alignment layers on a novel Langmuir trough using a flowing subphase. The surface morphology of PI LB film deposited on a graphite substrate was studied by atomic force microscopy. Experimental results give evidences that the polymer chains are oriented in the flow direction, along which LC molecules are aligned homogeneously. Thus the alignment of LCs may act through the orientation of PI molecules.

Keywords: Liquid crystal alignment, polyimide Langmuir–Blodgett films, flowing subphase, atomic force microscopy

1. INTRODUCTION

Recently there has been much interest in polyimide (PI) Langmuir–Blodgett (LB) films as rubbingless alignment layers for liquid crystal (LC) devices.[1–3] Compared with the conventional rubbing method the LB technique for LC alignment has a great advantage, e.g., it does not cause any contamination and electrostatic damage.[3–4] For surface stabilized ferroelectric LC devices using PI LB films as alignment layers the bistability can be improved and the threshold voltage can also be reduced[5–6] due to the uniform and ultrathin nature of LB films.[7] From a scientific point of view, LB technique enables us to make molecularly defined films to fit various purposes, and the alignment mechanism can thus be controlled and studied in detail. For example, it is known that the LC alignment on polymer films depends upon the uniform orientation of polymer molecules. This mechanism was first advanced by Castellano,[8] then later reinforced by Geary *et al.*[9] Other experimental evidences supporting such a mechanism have also been reported.[10,11] But the ordered polymer chains have never been observed directly, only deduced from other experimental data such as optical birefringence. Recently Fang *et al.*[12–13] and other researchers such as Baker *et al.*[2] have observed PI chains in LB films by scanning tunneling microscopy and Fang *et al.*[13] have still studied the anchoring structure of LC monolayer on PI LB films. Their observations support the alignment mechanism from an atomic-scale point of view.

The alignment ability of PI LB films comes from the ordered chain orientation and the ordered chain orientation can be ascribed to the dipping process.[12–15] In another system, Seki *et al.*[16] have found that the alignment property is related to the preparation method of the alignment layers. It seems difficult to align LCs on PI LB films prepared by a horizontal method because we do not know whether PI molecules are aligned uniformly and if aligned, in which direction the molecular chains are oriented. Furthermore, we do not know whether the molecules in each layer are aligned in the same direction. For practical use it is time-consuming to make LB films layer by layer by vertical dipping so that it is desirable to deposit the Langmuir monolayers horizontally and continuously to improve the deposition efficiency. Here we employ a novel system using a flowing subphase which has a capability for controlling the degree of the surface anisotropy and thus can meet the above requirements. Our novel LB method may be better than the rubbing and/or conventional LB method.

2. MATERIALS AND METHODS

The system to generate a homogeneous flowing subphase was designed by us. The main part of the system is a Langmuir trough, 165 cm in length, 7.5 cm in width, and 0.5 cm in depth. The schematic diagram of the trough is shown in Figure 1. A detailed description of the whole system has been reported elsewhere.[17]

Due to the lack of an amphiphilic nature of PI, we used a polyamic acid alkylamine salt (PAAS) as the precursor for preparing PI LB films. PAAS was 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 unit is 1.0 mM. The average molecular weight of polyamic acid is 4.0×10^4. The chemical structure of PI is given in Figure 2.

Double-distilled water fills the trough up to the rim of the trough. The flux was controlled at 0.03 lit./min. The PAAS solution was dropped onto the water surface at end A of the trough. A barrier was placed at end B of the trough to stop the

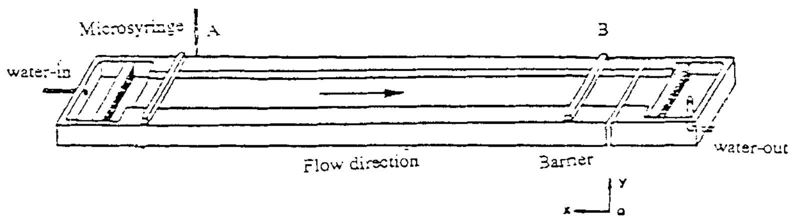

FIGURE 1 Schematic diagram of the Langmuir trough.

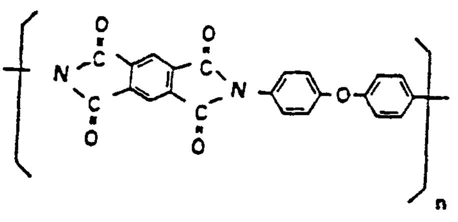

FIGURE 2 Chemical structure of the polyimide.

monolayer from floating away so that the monolayer can be compressed to a condensed state underneath by the flowing water. The distance between dropping the solution and placing the barrier was about 100 cm. All the experiments including the following atomic force microscopy (AFM) observation were performed in air and at room temperature (25°C).

The monolayer compressed before the barrier was transferred onto a highly oriented pyrolytic graphite (HOPG) and glass plates by horizontal lifting. HOPG was cleaned by adhesive tape to give an atomically flat surface. 5 layers of PAAS monolayer were deposited onto glass plates followed by a chemical treatment to convert PAAS LB films to PI films.[12] For AFM observation 1 layer was transferred. The AFM device, NanoScope III, was purchased from Digital Instrument Inc. at Santa Barbara. For AFM imaging in a contact mode the tip was positioned over the sample and scanned at a constant frequency. The force between the tip and the samples was less than 10^{-8} N by a feedback control.

The LC cell was assembled by sandwiching 4′-*n*-octyl-4-cyanobiphenyl (8CB) between two glass plates coated with PI LB films. 8CB filled the LC cell by capillary action when both the liquid crystal cell and 8CB were heated up to the clearing point of 8CB. The glass plates were placed parallel with regard to the flow directions and the distances of two plates were controlled at 20 μm by glass fibers. The LC cell was observed under polarized microscopy and the cell could be rotated in the plane vertical to the incident light.

3. RESULTS

Under crossed polarizing microscopy, the light intensity transmitted through the LC cell changed with a period of 90° when the cell rotated. When the flow direction is oriented at 0° with respect to the analyzer, the transmission is minimized. When the flow direction is oriented at 45° the transmission has a maximum value. This indicates that 8CB molecules are aligned homogeneously along the flow direction. Figure 3 is a photograph of the LC cell observed by polarized microscopy when the flow direction is oriented at 0° with respect to the analyzer. The alignment property does not change, no matter whether 8CB molecules are in the nematic phase or in the smectic phase.

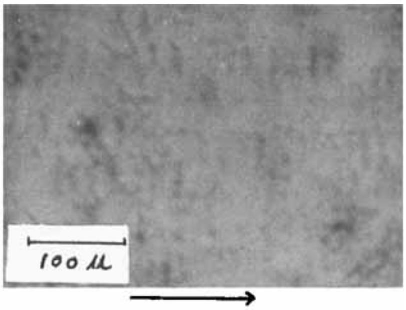

FIGURE 3 Photograph of liquid crystal cell observed by polarized microscopy. The flow direction is oriented at 0° with respect to the analyzer. The arrow indicates the flow direction.

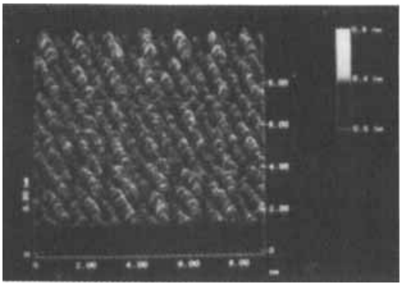

FIGURE 4 AFM image of polyamic acid alkylamine salt (PAAS) monolayer on HOPG. The higher regions correspond to PAAS chains. The arrow indicates the flow direction.

To understand the alignment mechanism, PAAS monolayer deposited on HOPG was characterized by AFM. Figure 4 shows a typical topographical image obtained. The image was stable when the sample was scanned repeatedly. The size of the graph is 9 nm by 9 nm. The periodic higher regions correspond to PAAS chains. The PAAS backbone is practically parallel to the flow direction. Measured from this figure, the space between two adjacent chains is about 7 Å. This value is close to that reported by others.[18] Other images obtained show a similar morphology, i.e., the polymer chains are almost aligned in the same direction. This indicates that PAAS chains are uniformly aligned in the flow direction.

It is reasonable to think that the chain orientation of PAAS retains after PAAS molecules change to PI molecules. Thus, the alignment of LCs on these PI LB films acts through the orientation of the polymer materials just as in other systems.

4. DISCUSSION

The uniform orientation of polymer chains in the alignment layer is essential for uniform LC alignment. In previous work, in order to make unidirectionally oriented polymer films, PAAS monolayers at the air–water interface were frequently deposited to solid substrates by a vertical method. The horizontal method was seldom used because of the reasons indicated in the introduction section. Here, the new Langmuir trough can not only compress the polymer monolayer, but also align the rod-like polymer molecules in the monolayer in the flow direction. Therefore, it is possible to deposit the Langmuir monolayer horizontally and continuously to solid substrates with a high deposition efficiency, resulting in anisotropic LB films.

Why are the polymer chains aligned in the flow direction? The physical origin of this alignment is understandable 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 Figure 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,[19] the velocity $v(y)$ of a steady laminar incompressible viscous flow inside two parallel stationary plates can be expressed as

$$v(y) = (y^2 - yd)/2\,\mu\cdot dp/dx,$$

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

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

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

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

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

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

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

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

And the shear force (per unit length) acting on 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 on 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 of arranging the molecular chains in the flow direction is very similar to the rubbing process.[9] Compared to the traditional rubbing process, the flow "rubs" the monolayer underneath in a two-dimensional space rather than in a three-dimensional space. Moreover, the rubbing strength can be easily controlled by monitoring the flux because the shear stress acting on the monolayer is flux-dependent (referring to Equation 3). Considering these factors we think that PI LB films may be better than rubbed ones.

5. CONCLUSION

To conclude, we have homogeneously aligned nematic and smectic liquid crystals on polyimide Langmuir–Blodgett films prepared by a horizontal method on a newly designed Langmuir trough using a flowing subphase. Atomic force microscopy investigation indicates that the new trough can compress the monolayer as well as align the molecular chains in the flow direction. This technique is similar to the rubbing process but with several exceptions.

Acknowledgements

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