Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Fang, J. Y. , Lu, Z. H. , Min, G. W. and Wei, Y.(1993) 'Investigation of alignment mechanism of liquid crystal on polyimide Langmuir-Blodgett films by scanning tunnelling microscopy', Liquid Crystals, 14: 6, 1621 — 1626
To link to this Article: DOI: 10.1080/02678299308027701
URL: http://dx.doi.org/10.1080/02678299308027701

LIQUID CRYSTALS, 1993, VOL. 14, NO. 6, 1621–1626

Investigation of alignment mechanism of liquid crystal on polyimide Langmuir–Blodgett films by scanning tunnelling microscopy

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The homogeneous alignment of a liquid crystal material, 4′-*n*-octyl-4-cyanobiphenyl (8CB), was achieved by polyimide Langmuir–Blodgett (LB) films. Scanning electron microscopy and scanning tunnelling microscopy measurements show that the alignment of the polyimide LB films with a grooveless surface occurs due to the orientation of the polyimide chains. We directly observe 8CB monolayers on oriented polyimide LB films. We find that the monolayers form a two dimensional crystalline structure and the 8CB molecules are always aligned along the chain direction of the polyimide. The results show that the alignment of 8CB molecules arises by an epitaxial growth on the oriented polyimide LB films.

1. Introduction

It is well-known that alignment of liquid crystal molecules strongly depends on the surface structures of the substrates [1]. Suitably treated substrates can induce alignment of liquid crystals, such as homeotropic alignment and homogeneous alignment, because of the anisotropic interfacial interaction between the liquid crystals and the substrates. In order to understand better the surface effect on the alignment of liquid crystals, many studies are focusing on the interfacial properties of liquid crystals.

Homogeneous alignment of liquid crystal molecules can be achieved by rubbed polyimide films. The alignment acts through parallel grooves produced by the rubbing process [2]. Recently Ikeno *et al.* [3] found that ultra-thin polyimide Langmuir–Blodgett (LB) films, without performing any rubbing process, could induce homogeneous alignment of ferroelectric liquid crystals. The discovery has attracted much attention, because surface stabilized ferroelectric liquid crystal cells using polyimide LB films as aligning layers show good bistability at low electric field. To understand the alignment mechanism of the polyimide LB films, it is necessary to observe directly the surface structures of the polyimide LB films and the anchoring structures of the liquid crystal molecules on the polyimide LB films.

Scanning tunnelling microscopy (STM) has come to be a promising technique for the elucidation of the structures of the LB films [4] and liquid crystal monolayers [5].

In this paper, we observed the alignment of liquid crystal molecules on ultrathin polyimide LB films. SEM and STM were used to examine the surface structures of the polyimide LB films and the anchoring structure of the liquid crystal monolayers. The experimental results give evidence implying that the alignment of the polyimide LB films acts through the orientation of the polyimide chain induced by the dipping process.

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2. Experimental details

LB films were prepared in a Langmuir trough. It is difficult to deposit polyimide films directly by the LB technique, because the polyimide molecule does not possess an amphiphilic nature. In our experiment, polyamic acid was used as a precursor for the polyimide. The deposition conditions for polyamic acid were as follows: polyamic acid was mixed with an alkylamine in an organic solvent. The mixture was spread on the water surface to form polyamic acid alkylamine salt monolayers. The monolayers were transferred onto solid substrates by a vertical dipping method at a surface pressure of $20\,\mathrm{mN\,m^{-1}}$. The dipping speed was $5\,\mathrm{mm\,min^{-1}}$. The polyamic acid alkylamine salt LB films (four molecular layers) were converted into polyimide LB films by chemical treatment [6].

The polyimide LB films were characterized by using STM and SEM. Highly oriented pyrolytic graphite (HOPG) substrates were cleaved by adhesive tape to give an atomically flat surface. The LB films were deposited on the HOPG substrates immediately after cleaving of the HOPG surfaces for SEM and STM observation.

A liquid crystal cell was assembled using two polyimide LB film coated glass plates with their dipping direction antiparallel. 4′-*n*-octyl-4-cyanobiphenyl (8CB) (Merck Ltd, U.K.) was used to fill the cell by capillary action. To minimize flow alignment effects, the filled cell was heated to give the isotropic phase, then slowly cooled from the nematic and then the smectic phases. The alignment of the 8CB in the cell was observed by polarizing optical microscopy.

To observe the first monolayer at the interfacial surfaces, we deposited 8CB monolayers on the polyimide LB films by the LB technique by virtue of the amphiphilic nature of the 8CB molecule. The sample in our experiments was prepared as follows: we spread 8CB, from a chloroform solution at a concentration of 1×10^{-3} M, on a subphase in a Langmuir trough. The subphase was double distilled water. To avoid the alignment action of vertical dipping, we deposited the 8CB monolayer on the polyimide LB film coated graphite substrates by horizontal lifting at a surface pressure of $3\,\mathrm{mN\,m^{-1}}$. The transfer ratio of monolayer can be determined by the decrease in the surface area occupied by the monolayer at the air–water interface. A low value of the surface pressure was chosen because at this pressure, 8CB molecules are able to lie flat on the water; this is the expected orientation when aligned by the polyimide layer. The sample was heated to the isotropic phase, and then cooled slowly to room temperature to make the 8CB molecules adsorbed on the surface of the polyimide LB films give alignment.

The STM tip was scanned at a constant tunnel current of 0·2 nA. All STM images were taken in air at room temperature. The bias voltage was in the range from 0·8 to 1·2 V (tip positive).

3. Results and discussion

Figure 1 shows the surface pressure–area isotherm of the polyamic acid alkylamine salt monolayer. The limiting area per monomer unit calculated from the isotherm was 93 Å^2. This value agrees well with that obtained from a molecular model (100 Å^2) and indicates that the molecular chains of polyamic acid lie flat at the air–water interface, and the alkylamine chains rest on the flat chains of polyamic acid.

The SEM image of the polyimide LB film is shown in figure 2. As can be seen the polyimide LB film has a uniform structure on a macroscopic scale. STM examination indicates that the polyimide LB film has an ordered structure on the molecular scale, as shown in figure 3. The polyimide molecular chains are oriented in the dipping direction

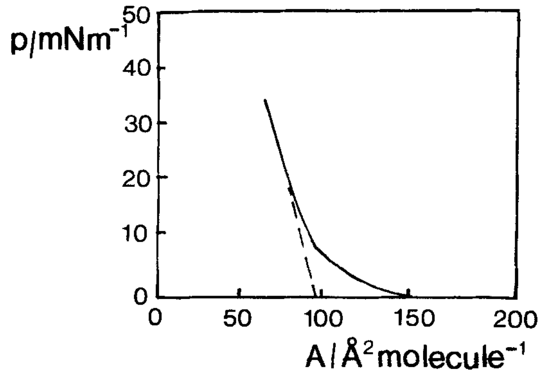

Figure 1. Surface pressure–area (p–A) isotherm of polyamic acid alkylamine salt monolayer (polyamic acid : alkylamine = 1 : 2).

Figure 2. SEM image of polyimide LB film deposited HOPG substrate.

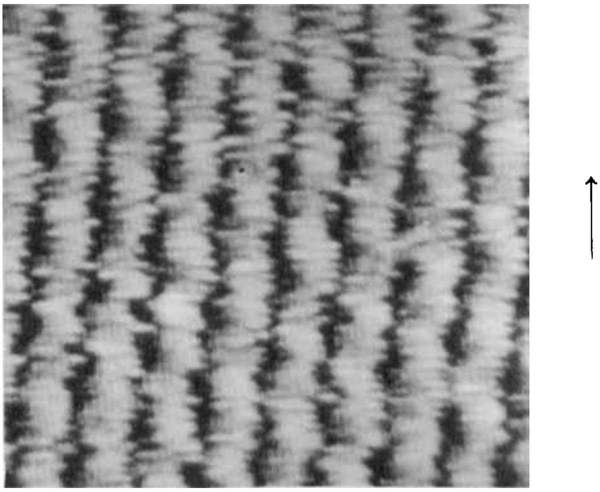

Figure 3. STM image of polyimide LB film deposited HOPG substrate (60 Å × 60 Å). The arrow shows the deposition direction of the LB film.

and the chain diameter is in the range 5 to 6 Å. We suggest that the orientation of the polyimide chains is induced by the dipping process.

Under microscopy with crossed polarizers, a uniform alignment is observed. From the photograph of the liquid crystal cell shown in figure 4, we note that the nematic layer has a distinct interface between the polyimide LB film coated region and the bare region. In the bare region, the field of view is not uniform; many domains are visible, indicating that the molecular director of the liquid crystal varies randomly in his region, while in the polyimide LB film coated region, the field of view is uniform. The intensity of light transmission in the polyimide LB film coated region changes periodically with rotation of the liquid crystal cell. When the dipping direction is oriented at 0° with respect to the analyser, the transmission of the liquid crystal cell is zero. When the dipping direction is oriented at 45° with respect to the analyser, the transmission of the liquid crystal cell is 95 per cent. Extinction occurs every 90°. The experimental error in our apparatus is about ±0·5°. This indicates that the liquid crystal molecules are aligned homogeneously with the dipping direction. This homogeneous alignment remains even when the sample is cooled to the smectic phase.

Figure 5 shows the surface pressure–area curve for 8CB at 20°C. We find that 8CB forms monolayers at the air–water interface. At a surface pressure of $3\,\mathrm{mN\,m^{-1}}$, the area per molecule is about $65\,\text{Å}^2$. This value is much larger than the cross-sectional area of 8CB. The monolayer at $3\,\mathrm{mN\,m^{-1}}$ may be considered to be in a two dimensional liquid expanded state. In this state, the orientation of the 8CB molecules is random at the air–water interface.

Figure 6 shows the STM image of 8CB monolayers adsorbed on the surface of the oriented polyimide LB film. The 8CB molecules form a two dimensional crystalline structure. The bright regions represent the location of the cyanobiphenyl groups, and the dark regions correspond to the alkyl chains, because the conductivity of the cyanobiphenyl group is higher than that of the alkyl chains. As can be seen in figure 6, the width of the bright region is 21 ± 1 Å; this value is nearly two times the length of the

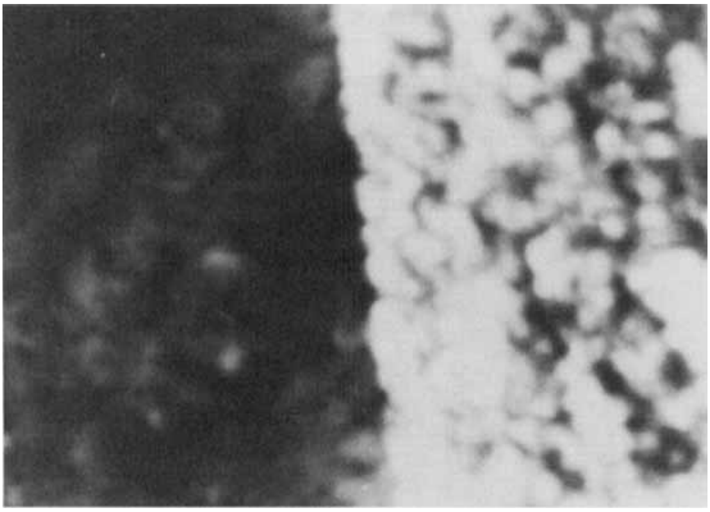

Figure 4. Photograph of a liquid crystal cell. The dipping direction oriented at 0° with respect to the analyser. Crossed polarizers. Left side: the polyimide LB film coated region; right side: the bare region.

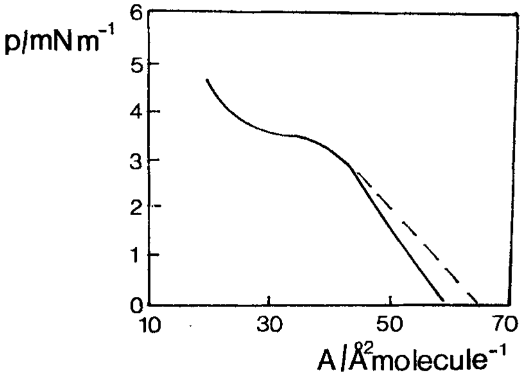

Figure 5. Surface pressure–area (p–A) curve of 8CB monolayer at 20°C.

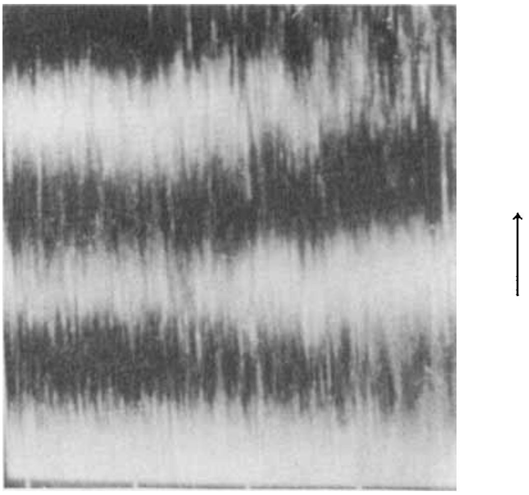

Figure 6. 80 Å × 100 Å STM image of the 8CB monolayer adsorbed on graphite covered by the polyimide LB film. The arrow shows the chain direction of the polyimide.

cyanobiphenyl head group (12 Å, see [7]). This indicates that the arrangement of the 8CB molecules is a head-to-head and tail-to-tail model. The smectic layer spacing of 8CB on the surface of the oriented polyimide LB film is 40 ± 1 Å; this value indicates that the cyano groups of the 8CB molecules are very slightly interdigitated. By changing the dipping direction, we control the polyimide molecular chains in the LB films. But the 8CB molecules are always oriented along the direction of the polyimide chains.

Why do the polyimide LB films induce a homogeneous alignment in liquid crystal films? Using SEM, we do not find any evidence of grooves in the polyimide LB film surface (see figure 2). But using STM, we find the polyimide molecular chains are oriented in the dipping direction (see figure 3). The results indicate that the alignment of 8CB on the oriented LB film comes from the interaction of oriented polyimide chains and alkyl chains. The alignment action of oriented polymers on liquid crystal molecules has been well-established through previous experiments [8,9]. Therefore we suggest that the alignment of 8CB molecules arises through an epitaxial growth on an oriented polyimide LB film.

4. Conclusion

The alignment mechanism of liquid crystal molecules on polyimide LB films has been investigated. We find that the polyimide chains are oriented by the dipping process. 8CB monolayers adsorbed on oriented polyimide LB films form a two dimensional crystalline structure and the 8CB molecules are oriented along the polyimide molecular chains. The interactions between oriented polyimide chains and liquid crystal molecules induce a homogeneous alignment in the liquid crystal layers. The results demonstrate that the alignment of 8CB arises by an epitaxial growth on an oriented polyimide LB film.

We are grateful to Merck Ltd, U.K., for supplying the liquid crystal sample and the Shanghai Jiaotong University for supplying the polyimide precursor. The work was supported by the National Natural Science Foundation of China.

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