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Investigation of Alignment Mechanism of Polyimide Langmuir-Blodgett Films on Liquid Crystal

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The homogeneous alignment of liquid crystals, 4′-n-octyl-4-cyanobipheny(8CB), was achieved by polyimide Langmuir-Blodgett(LB) films. The surfaces of the polyimide LB films were examined by scanning electron microscopy and scanning tunneling microscopy. Experimental results indicate that the alignment of the polyimide LB films with grooveless surfaces occur due to the orientation of polyimide chains.

Keywords: homogeneous alignment of liquid crystal, polyimide Langmuir-Blodgett films

1. INTRODUCTION

It is well known that alignment of liquid crystal molecules strongly depends on the surface structures of the substrates.[1] Homogeneous alignment of liquid crystal molecules can be achieved by rubbed polyimide films. The alignment acts through parallel groovers produced by the rubbing process.[2] Recently Ikeno et al[3] found that the ultrathin polyimide Langmuir-Blodgett (LB) films without performing rubbing process could induce homogeneous alignment of ferroelectric liquid crystals. The discovery has attracted much attention, because the surface stabilized ferroelectric liquid crystal cells using polyimide LB films as aligning layers show a good bistability at a low electric field. To understand the alignment mechanism of the polyimide LB films, it is necessary to directly observe the surface structures of the polyimide LB films from macroscopic to molecular scales. Scanning electron microscopy (SEM)[4] and scanning tunneling microscopy (STM)[5] have shown to be promising techniques for the elucidation of the structures of the LB films.

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

2. EXPERIMENTAL DETAILS

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

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 HOPG substrates immediately after cleaving of HOPG surfaces for SEM and STM observation.

Liquid crystal cell was assembled using two polyimide LB film coated glass plates with their dipping direction antiparallel. 4'-n-octyl-4-cyanobipheny (8CB) (BDH chemical Ltd) was filled the cell by capillary action. To minimize flow alignment effect, the cell filled was heated to the isotropic phase, then slowly cooled to nematic and smectic phases. The alignment of 8CB in the cell was observed with a polarizing microscopy.

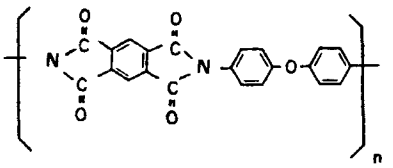

FIGURE 1 Chemical structure of polyimide

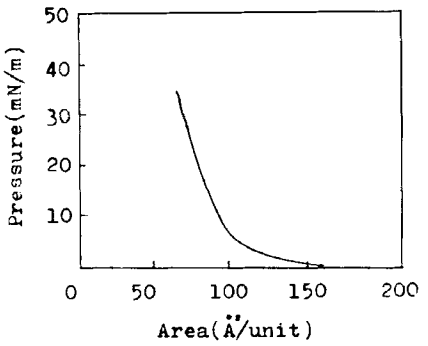

FIGURE 2 Surface pressure-area isotherm of polyamic acid alkylamine salt monolayer. (polyamic acid: alkylamine = 1:2)

3. RESULTS AND DISCUSSION

Figure 2 shows the surface pressure-area isotherm of 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 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.

SEM image of polyimide LB film is shown in Figure 3. As can be seen the polyimide LB film has uniform structure on a macroscopic scale. STM examination

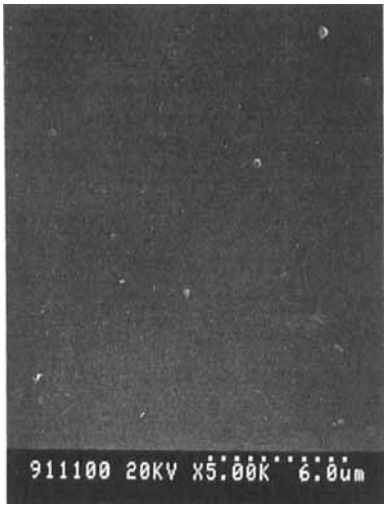

FIGURE 3 SEM image of polyimide LB film deposited on HOPG substrate

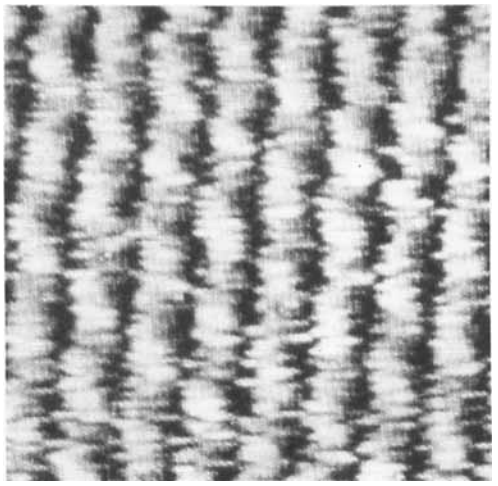

FIGURE 4 STM image of polyimide LB film deposited on HOPG substrate (60 Å · 60 Å)

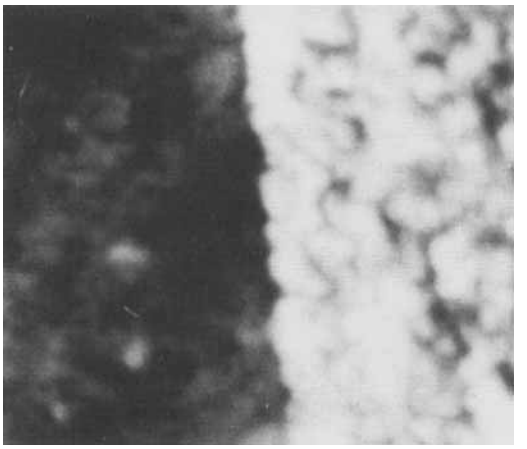

FIGURE 5 Photograph of liquid crystal cell. The dipping direction oriented at 0° with respect to the analyser. Crossed polarizers. Left side: the polyimide LB film coated region. Right side: the bare region.

indicates that the polyimide LB film has an ordered structure at molecular scale, as shown in Figure 4. The molecular chains of polyimide are oriented in the dipping direction and the chain diameter is in the range of 5 to 6 Å. We suggest that the orientation of polyimide chains is induced by the dipping process.

Under the microscopy with crossed polarizers, the uniform alignment is observed. From the photograph of the liquid crystal cell shown in Figure 5, we note that nematic layer have a distinct interface betwen polyimide LB film coated region and bare region. On bare region, the field of view is not uniform. Many domains are visible, indicating the director of liquid crystal molecules varies randomly in the region. While on polyimide LB film coated region, the field of view is uniform. The intensity of transmission light in the polyimide LB film coated region changes periodically with the 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%. The extinctions occur every 90°. The experimental error of our apparatus is about 0.5°. This indicates that liquid crystal molecules are aligned homogeneously with the dipping direction. This homogeneous alignment remains even when the sample is cooled to smectic phase.

Why do the polyimide LB films induce an homogeneous alignment in liquid crystal layers. Using SEM, we do not find any evidence of grooves in the polyimide LB film surface (see Figure 3). But using STM, we find the molecular chains of polyimide are oriented at the dipping direction. So we suggest that the alignment of the polyimide LB films on liquid crystal molecules acts through the orientation of polyimide chains. This alignment mechanism was presented by Castellano[7] and supported by some experimental results in other systems.[8] In addition, the ability of STM to image the polyimide LB films demonstrates that electrons from graphite

can be transferred through the polyimide LB films. They may contribute to neutralizing and discharging the accumulated surface charges. We suggest that the existence of electron tunneling in the polyimide LB alignment films is very useful to produce good electrooptic effects in liquid crystal cells.

4. CONCLUSION

Using SEM and STM, we have investigated the alignment mechanism of polyimide LB films on liquid crystal molecules. The experimental results indicate that the polyimide chains are oriented by the dipping process. The interactions between oriented polyimide chains and liquid crystal molecules induce an homogeneous alignment in the liquid crystal layers.

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