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J. Y. Fang^a, Z. H. Lu^a, Y. Wei^a & P. Stroeve^b

^a Laboratory of Molecular and Biomolecular Electronics,
Southeast University, Nanjing, 210018, P. R., China

^b Department of Chemical Engineering, University of California,
Davis, California, 95616, U.S.A.

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J. Y. FANG, Z. H. LU and Y. WEI

Laboratory of Molecular and Biomolecular Electronics, Southeast University, Nanjing, 210018, P. R. China

and

P. STROEVE

Department of Chemical Engineering, University of California, Davis, California 95616, U.S.A.

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The pyrolyzed polyimide Langmuir-Blodgett film can provide an aligning layer and an electrode for liquid crystal cells. The LB film surface is characterized by Scanning electron microscopy, scanning tunneling microscopy and optical absorption spectra. We find that the aligning and conducting mechanism is due to the presence of carbon enriched islands in the LB film. The electrooptical effects in twisted nematic liquid crystal cells using the films as electrodes and aligning layers are observed.

Keywords: *homogeneous alignment of liquid crystal, pyrolyzed polyimide Langmuir-Blodgett films and electrooptical effect*

1. INTRODUCTION

The alignment of liquid crystals on solid substrates is a very important problem in both fundamental physical studies and practical applications. The subject of the alignment of liquid crystals has been actively studied over the past decade. Many specific materials have been used as aligning films for controlling the alignment of liquid crystals. Since Forster *et al.*¹ found that highly oriented pyrolytic graphite (HOPG) shows strong aligning ability for liquid crystals, many active studies have been conducted for understanding the alignment mechanism of the highly conductive film for liquid crystals.^{2–5}

Recently, we reported an ultrathin conductive film by the pyrolysis of a polyimide Langmuir-Blodgett film (LB).⁶ We wanted to know whether the pyrolyzed polyimide LB film can be used as both the electrode and the aligning layer of liquid crystal cells. In this paper, we report some experimental results on the alignment of liquid crystal molecules on the conductive film. A possible alignment mechanism

is proposed based on the characterization results for the pyrolyzed polyimide LB film.

2. EXPERIMENTAL METHODS

A polyimide, with its chemical structure shown in Figure 1, was diluted in 1:1 mixture solvent of *N,N*-dimethylacetamide and benzene in a concentration of 0.15 mg/ml. A Langmuir trough was used to prepare polyimide monolayers. The sub-phase was double distilled water. Quartz plates were used as the substrates to deposit the polyimide Langmuir-Blodgett film (100 monolayers). The pyrolysis of the polyimide LB film was carried out at 1000°C in a clean hydrogen oven for 60 min. The UV-Visible absorption spectra of the LB films were measured with a DU-8B spectrophotometer. The scanning electron microscope (SEM) images were taken with a X650 SEM operating in the secondary electron emission mode. The scanning tunneling microscope (STM) used in the study was a commercial instrument (NanoScope, Digital Instruments). The STM tip was positioned over the LB films and scanned at a constant tunnel current of 0.2 nA. All STM images were taken in air and at room temperature. The bias voltage was in the range from 0.8 to 1.2 V (tip positive).

In our experiment, liquid crystal cells were assembled using two pyrolyzed polyimide LB film, coated quartz plates with a 25 µm Mylar spacer. The two substrates were arranged with their dipping direction antiparallel or parallel. The cells were filled with a nematic liquid crystal 5CB (4'-*n*-pentyl-4-cyanobiphenyl) in the isotropic phase. The alignment of liquid crystal molecules was observed with a Leitz (ORTHOPLA-POL) polarizing optical microscopy at room temperature. The change of a transmission light (He-Ne laser: 632.8 nm) intensity through the cells by applied voltage was measured by a photomultiplier.

3. RESULTS AND DISCUSSIONS

The absorption spectra of the polyimide LB film and the pyrolyzed polyimide LB film are shown in Figure 2. As can be seen the two absorption bands of polyimide LB film (A) at 220 nm and 280 nm disappear after the pyrolysis, and a broad band with a maximum peak at 270 nm is visible (B). This indicates that a carbon aggregate is formed by the pyrolysis of the polyimide LB film. Figure 3 shows the SEM image

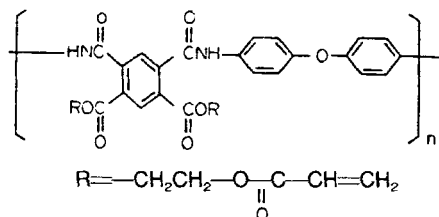


FIGURE 1 Chemical structure of polyimide.

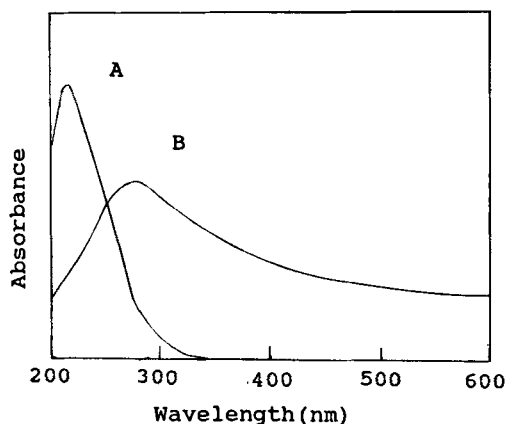


FIGURE 2 Absorption spectra of polyimide LB film (A) and pyrolyzed polyimide LB film (B).

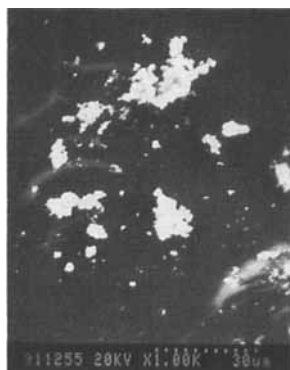


FIGURE 3 SEM image of pyrolyzed polyimide LB film.

of the pyrolyzed polyimide LB film. From separate SEM studies (not shown), the polyimide LB film has a smooth surface. After the pyrolysis, island structures form in the LB film surface. Burger *et al.*⁷ have demonstrated that oxygen, hydrogen and nitrogen are released in molecular fragments (CO , CO_2 , H_2 and N_2) during the pyrolysis of polyimide by chemical analysis. This will lead to the rearrangement of the enriched carbon. We suggest that the islands are aggregates of enriched carbon. Figure 4 shows the STM image of an aggregate. We find that the aggregate consists of parallel bright stripes separated by dark regions. The orientation of the bright stripes is rough parallel to the dipping direction of the substrate. The bright region corresponds to carbon, because carbon has high conductivity. As can be seen from Figure 4, carbon aggregate has a two-dimensional crystalline structure with a lattice of 2.8 \AA .

We have found that the polyimide LB film is insulating, while the pyrolyzed polyimide LB film shows a conductivity as high as 200 S/cm . The conductivity may be contributed to a carbon enriched aggregate produced by the pyrolysis at higher temperature. Venkatesan *et al.*⁸ have demonstrated that an electronic hopping

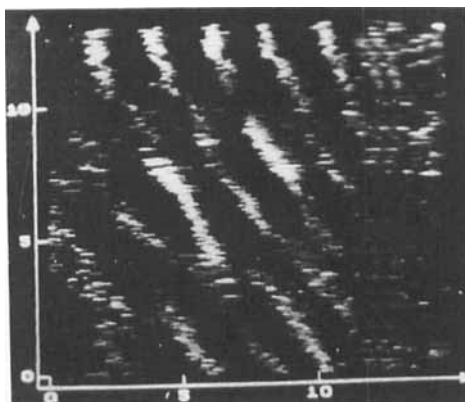


FIGURE 4 STM image of pyrolyzed polyimide LB film. Distances are in Angstroms.

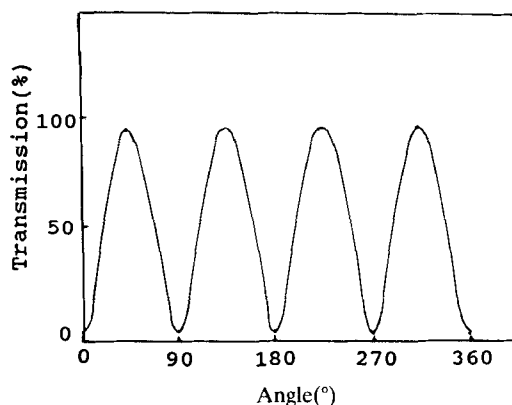


FIGURE 5 Transmission light intensity as a function of rotational angle of the microscope with crossed polarizers.

process between islands embedded in an insulating matrix is mainly due to a conductive mechanism.

Ong *et al.*⁹ demonstrated that inhomogeneous surfaces containing island structures of known materials having aligning forces could control liquid crystal orientation. Therefore, the pyrolyzed polyimide LB film containing carbon enriched islands should also control liquid crystal orientation.

Figure 5 shows the transmitted light intensity of the liquid crystal cell as a function of the rotational angle of the polarizing microscopy with the crossed polarizers. When the dipping direction is oriented at 0 with respect to the analyser, the transmission is 5%. When the dipping direction is oriented at 45 with respect to the analyser, the transmission is 90%. The extinctions occur every 90°. This indicates that the 5CB molecules are aligned homogeneously along the dipping direction.

McGonigal *et al.*¹¹ have demonstrated that alkyl chains of the liquid crystal (5CB) can be aligned by the lattice of HOPG. From our point of view, the alignment of 5CB molecules can be understood as follows: The surfaces of the pyrolyzed po-

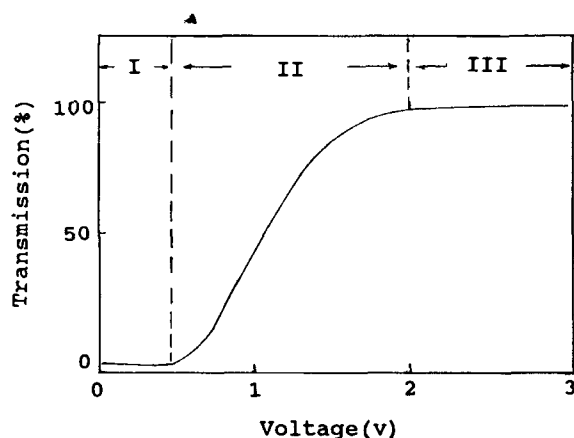


FIGURE 6 The voltage dependence of the transmission in the TNLC cells with parallel polarizers.

lyimide LB films form graphite-like structures with a lattice spacing of 2.8 \AA , as shown in Figure 4. The registry of alkyl chain of the 5CB molecule with the graphite lattice leads to the homogeneous alignment of the 5CB molecules. Considering the size of the lattice spacing, it may be inferred that the 5CB molecules suitably aligned perpendicular to the lattice vector. The proposed alignment model is in good agreement with our experimental results.

Based on the results, we fabricated the twisted nematic liquid crystal (TNLC) cells by using the pyrolyzed polyimide LB films as electrodes and aligning layers. When no voltage is applied to the electrodes, the conoscopic image for the TNLC cells between parallel polarizers appears completely dark. This indicates that liquid crystal molecules rotate incident light by 90° . When 5 volts are applied to the electrodes, the conoscopic image for the TNLC cells between perpendicular polarizers is a dark cross against a white background. This indicates that the nematic layer becomes optically uniaxial. The nematic director in the center of the TNLC cells is aligned parallel to the electric field, that is, perpendicular to the pyrolyzed polyimide LB film surfaces.

Figure 6 shows the voltage dependence of the transmission in the TNLC cells with parallel polarizers. When the voltage increases from zero, the response is as follows. There are obviously three regions I, II and III. The transmission is 3% in region I and increases in region II. The transmission saturates in region III. The threshold voltage is 0.7 V.

4. CONCLUSION

We have demonstrated that the pyrolyzed polyimide LB films can induce the homogeneous alignment of liquid crystal molecules. Scanning electron microscopy and scanning tunneling microscopy show that the pyrolyzed LB film surfaces form carbon aggregates. The aligning force of the pyrolyzed LB films for liquid crystal molecules comes from the registry of alkyl chains of the liquid crystal molecules with the lattice of carbon aggregates. The twisted nematic liquid crystal cells using

the pyrolyzed polyimide LB films as electrodes and aligning layers show good electrooptical effects.

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