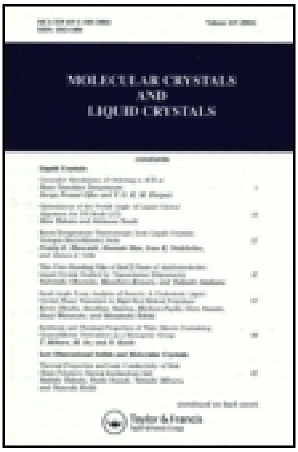

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The Pretilt Angle Controllable Polyimide Langmuir-Blodgett Film for Nematic Liquid Crystals

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The Pretilt Angle Controllable Polyimide Langmuir-Blodgett Film for Nematic Liquid Crystals

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A new non-rubbing alignment film for nematic liquid crystals has been developed employing the polyimide precursor Langmuir-Blodgett film having long chain alkyl groups. This film has the ability to tilt the liquid crystal molecules.

We discovered that the pretilt angle of nematic liquid crystals can be controlled by changing the thermal treatment temperature of the polyimide precursor Langmuir-Blodgett films. We studied the causing mechanism of the pretilt angle by investigating the thermal treatment temperature dependence of degree of imidization, the number of the long chain alkyl groups, the critical surface tension, and the tilt angle of long chain alkyl groups of the Langmuir-Blodgett films.

Keywords: Langmuir-Blodgett films, polyimide, alkyl groups, nematic liquid crystals, alignment film, pretilt angle, critical surface tension, degree of imidization

1. INTRODUCTION

Recently, the technical development of liquid crystal display (LCD) devices has made remarkable progress. In particular, the display characteristic has been improved by employing active matrix devices.

In liquid crystal cells, the liquid crystal molecules are sandwiched with glass plates, and the molecules must be aligned. For this purpose, the inside surfaces of the plates are treated to align the liquid crystal molecules. There are various kinds of surface treatment methods. Generally, alignment is obtained by a rubbing technique which is rubbing thin films of polyimide with cloth. This technique is suitable for mass production and stability of alignment. But there are two problems in the rubbing technique; one is generation of dust and the other is static electricity. These cause degradation of thin film transistor (TFT) devices. Therefore non-rubbing techniques are indispensable for TFT devices. We chose to study the polyimide Langmuir-Blodgett (LB) technique from several non-rubbing alignment techniques. The LB films were transferred onto the substrate from the monolayers on the surface of water.

Several reports, applying LB films to liquid crystal alignment techniques have been published by several research groups.[1,2,3,4,5] They found that the main chains of the LB films were oriented in the same direction as the lifting substrate and the LB film align liquid crystal molecules. However, twisted nematic (TN) and super twisted nematic (STN) LCDs using these LB films have alignment defects, such as reverse twist and reverse tilt disclinations caused by the LB films' inability to pretilt the liquid crystal molecules.[2,3]

The objective of this work is to add to the LB films' capability to tilt liquid crystal molecules. In this paper, we discuss the details of this pretilt angle control technique, and the causing mechanisms of the pretilt angle.

2. EXPERIMENTS

A) Synthesis of the LB Material

The polyimide precursor (PIP) used in this work is shown in Figure 1. The PIP was synthesized as described in previous papers.[1,6]

B) Preparation of the LB Films

Monolayers of the PIP were formed by spreading a solution of PIP dissolved in chloroform-dimethylacetamide in a 4:1 volume ratio onto purified water at the subphase temperature of 20°C, and compressing the surface pressure to 20 dyn/cm. Transfer of the monolayers onto ITO-coated glass substrates and Si wafers were carried out at the dipping speed of 10 mm/min, 11 layers were built up onto the ITO)-coated glass substrates, and 41 layers onto Si wafers. The Joyce-Loebl Trough (Model 4) was used to prepare the LB films. The films were the Y-type.

The transformation of the polyimide LB (PI-LB) films was obtained by heating the PIP-LB films transferred substrates for 1 hour. The reaction scheme is shown in Figure 2.

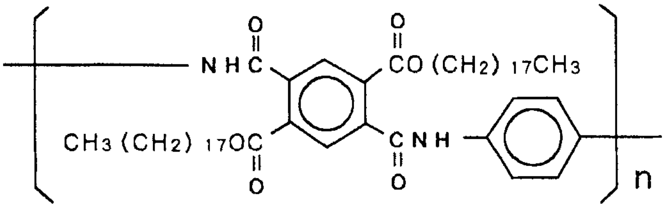

FIGURE 1 Structure of PIP.

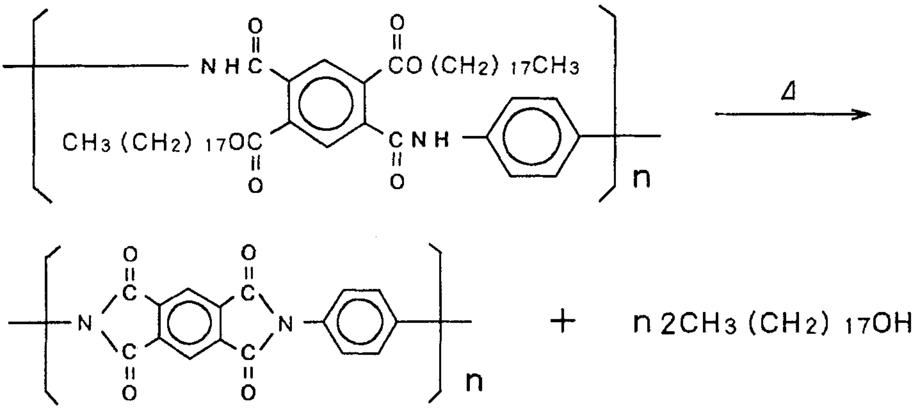

FIGURE 2 Scheme showing the PIP → PI reaction.

C) Evaluation of the Liquid Crystal Molecules' Alignment

a) Measurement of the liquid crystal molecules' pretilt angle. Antiparallel cells were fabricated to evaluate the pretilt angle. The cells were fabricated by two glass substrates arranged in an antiparallel direction from lifting, gapped at 20 μm, and filled with ZLI-3405. The pretilt angles were measured by two methods: the crystal rotation method (0 ~ 10 degree) and the magneto capacitive null method (0 ~ 90 degree).

b) Observation of the alignment. TN cells were fabricated to evaluate the alignment state. The cells were fabricated by two glass substrates arranged in a cross direction from lifting, gapped at 9 μm, and filled with Merck ZLI-3405 containing 1 wt% of c-15. The reverse twist and tilt disclinations were observed with a polarizing microscope.

D) Evaluation of the LB Films

a) Estimation of the degree of imidization and the number of the octadecyl groups. The degree of imidization and the number of the octadecyl groups were estimated by measuring the IR absorbance of the imide rings (C—N stretching vibration) and the octadecyl groups (C—H stretching vibration) using KBr pellets of the PIP.

The degree of imidization and the number of the octadecyl groups in the PIP thermally treated at several temperatures were estimated under the assumption that without thermal treatment the degree of imidization was 0% and the number of the octadecyl groups was 2 N/unit (N means the number of the octadecyl grups) and with 400°C thermal treatment the degree of imidization was 100% and the number of the octadecyl groups was 0 N/unit.

b) Estimation of the critical surface tension. The critical surface tensions were obtained by the Zisman plot. The plotted values are the contact angles of chemical organic solvents on the LB films on the ITO-coated glass substrate. The organic solvents used were water, diiodomethane and formamide.

c) Estimation of the tilt angle of the octadecyl groups. The tilt angle of the octadecyl groups of the LB films from the substrate were estimated by two methods: measuring the thickness, and the IR absorbance of the LB films on the Si wafer.

The thickness of the LB films was measured by the ellipsometry method. The tilt angle of the octadecyl groups of the LB films was estimated from the measured thickness and the molecular model.

The IR absorbance of the octadecyl groups of the LB films was measured by the transmittance method and the RAS method. The tilt angle of the octadecyl groups was estimated from Umemura's method.[7]

3. RESULTS

A) Alignment of the Liquid Crystal Molecules on the LB Film

There is a strong relationship between the alignment of liquid crystal molecules and the degree of alignment of the LB film. Since the PIP-LB films are highly oriented, the liquid crystal molecules on the PIP-LB films align very well.[1] According to the study using the Guest-Host liquid crystal, the liquid crystal molecules are oriented in the same direction as the lifting substrate.[8]

B) Pretilt Angle of the Liquid Crystal Molecules

Temperature dependence of the pretilt angle is shown in Figures 3 and 4. When thermal treatment is below 175°C, the pretilt angle of the liquid crystal molecules is above 65°. In the case of thermal treatment above 200°C, the pretilt angle of the liquid crystal molecules is 0°. In the case of thermal treatment at about 185°C, the pretilt angle changes drastically.

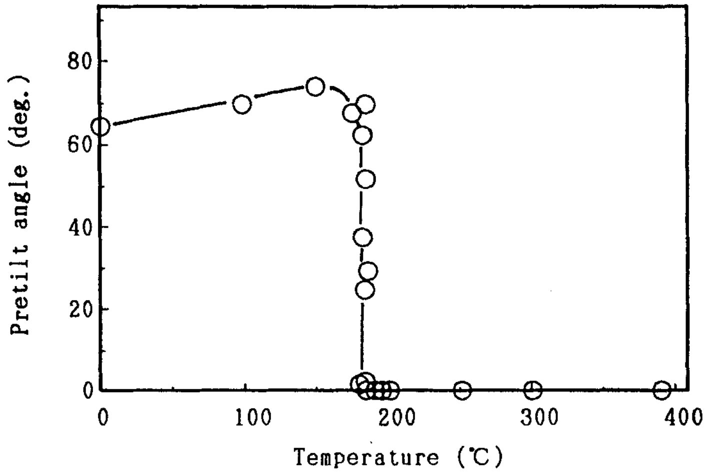

FIGURE 3 Temperature dependence of the pretilt angle (1).

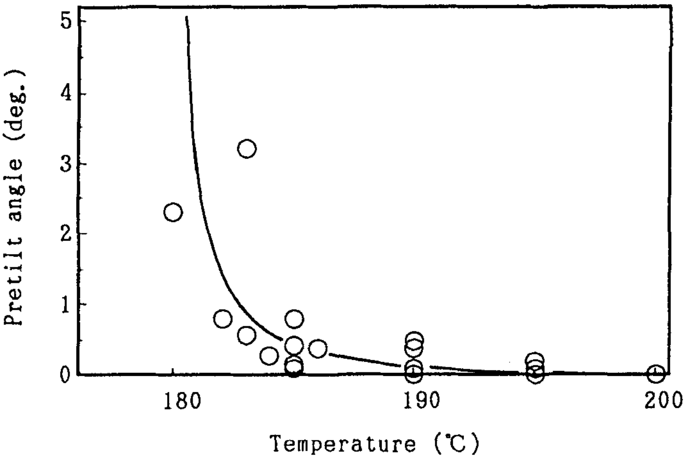

FIGURE 4 Temperature dependence of the pretilt angle (2).

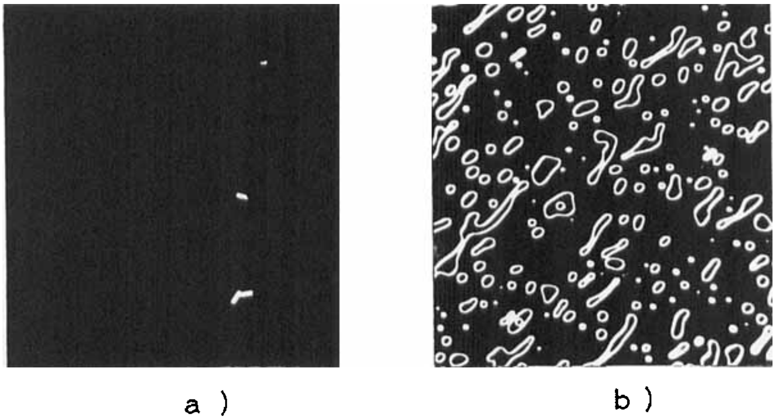

FIGURE 5 Polarizing microscope photographs of TN cells. a) at 185°C, b) at 250°C ($V > 0$).

C) Alignment of the Liquid Crystal Molecules of the TN Cells

The polarizing microscope photographs of TN cells are shown in Figure 5. When thermal treatment is not applied, the liquid crystal molecules aligned almost homeotropically. In the case of thermal treatment at 250°C, the liquid crystal molecules' alignment is perfectly homogeneous and there are reverse tilt disclinations when an electric field is applied (50 Hz, $V_{\text{eff}} = 6$ V). In the case of thermal treatment at 185°C, the liquid crystal molecules aligned homogeneously without reverse twist and tilt disclinations.

D) Property of the LB Films

Temperature dependence of the number of the octadecyl groups and the degree of imidization are shown in Figure 6. As the thermal treatment temperature in-

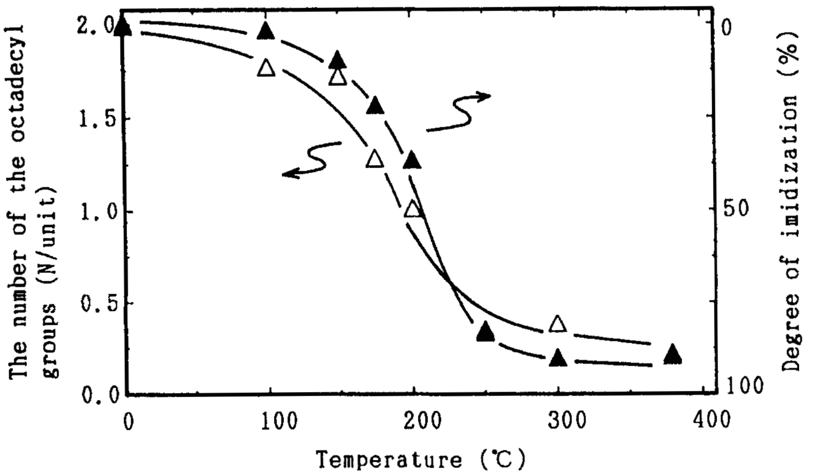

FIGURE 6 Temperature dependence of the number of the octadecyl groups and the degree of imidization.

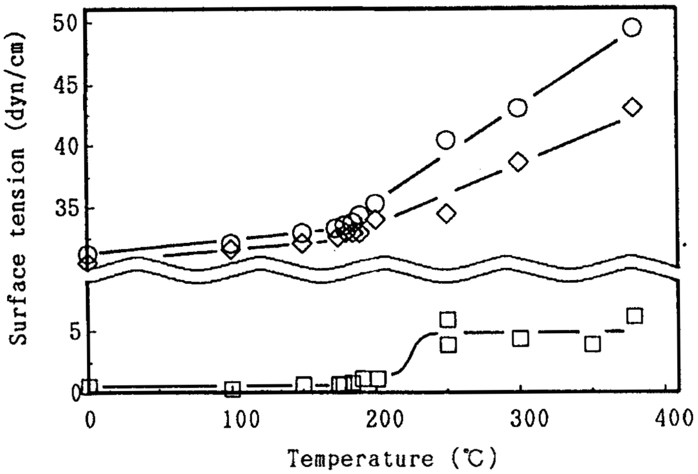

FIGURE 7 Temperature dependence of the surface tension (dyn/cm). ○: Critical surface tension, ◇: Dispersion force component, □: Polarity force component.

creases, the degree of imidization increases and the number of the octadecyl groups decreases. The two isotherms in Figure 6 are very similar. It shows that the octadecyl groups extracted from the PIP by imidization reaction are completely removed from the LB films. The imidization reaction occurs drastically between temperature 150°C and 250°C.

Temperature dependence of the surface tension is shown in Figure 7. The critical surface tension increases drastically at the thermal treatment temperature of about above 200°C, especially the polarity force component.

Temperature dependence of the tilt angle of the octadecyl groups is shown in Figure 8. The two results, which were obtained from the measurement of the

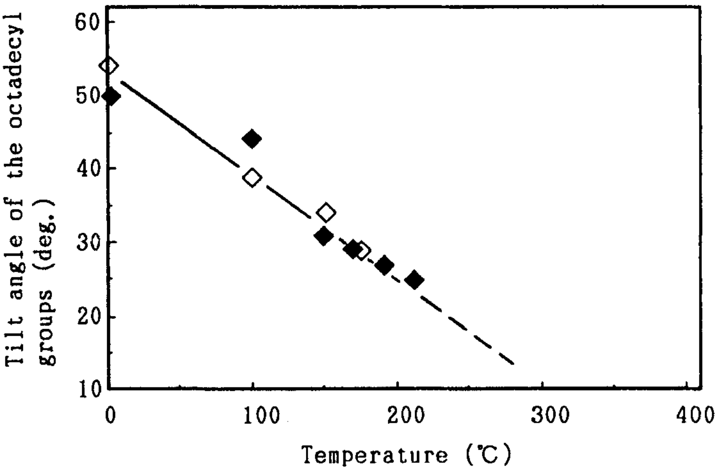

FIGURE 8 Temperature dependence of the tilt angle of the octadecyl groups. ◇ : IR, ◆ : Thickness.

thickness and the IR absorbance, are in good agreement. As the thermal treatment temperature increases the tilt angle of the octadecyl groups decreases linearly.

4. DISCUSSION

From the result, we suppose that the control mechanism of the pretilt angle is as below.

The octadecyl groups have the ability to align homeotropically, and the main chains of polyimide have the ability to align homogeneously. Therefore, controlling the pretilt angle can be achieved by controlling the number of the octadecyl groups of the films, which control the balance of alignment forces of homeotropic and homogeneous. The number of the octadecyl groups can be controlled by the treatment temperature.

On the basis of this scheme, we explain the details of the relationship between the pretilt angle of liquid crystal molecules and the properties of PI-LB films as shown in Figure 9. The figures in Figure 9 are not for the LB films—liquid crystal molecules interface but for bulk.

When thermal treatment is not applied, the octadecyl groups of the films protrude densely from the surface of the films at an unusually large angle of 65° as shown in Figure 9a. Consequently, the critical surface tension of the film is very small and thus the liquid crystal molecules aligned almost homeotropically.

In the case of thermal treatment at 175°C (as shown in Figure 9b), the number of the octadecyl groups of the films decreased more than when thermal treatment is not applied. Therefore, the tilt angle of the octadecyl groups from the substrate decreased. But there is no critical surface tension change, hence we suppose that the surface of the films is still covered with many octadecyl groups. Consequently, the liquid crystal molecules alignment remained nearly homeotropic.

In the case of thermal treatment at 185°C (as shown in Figure 9c), the number

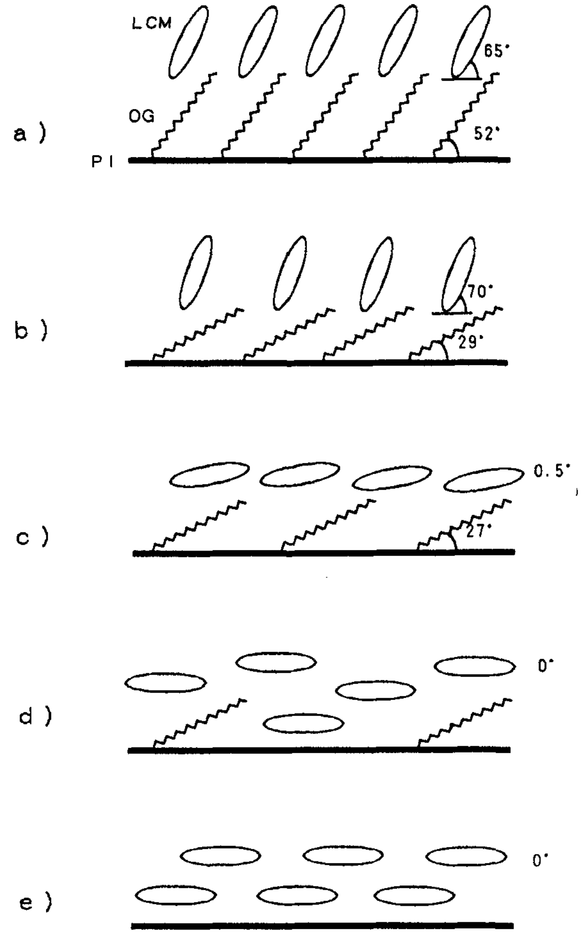

FIGURE 9 The alignment model of temperature dependence of the liquid crystal molecules (LMC), the octadecyl groups (OG) and the main chain of the polyimide (PI). The pretilt angle and the octadecyl group's tilt angle are shown in the figure. a) non thermal treatment, b) at 175°C, c) at 185°C, d) at 200°C, e) at 380°C.

of the octadecyl groups decreased more than that of at 175°C. The polyimide's main chain becomes effective to the liquid crystal molecules. At 185°C, the liquid crystal molecules aligned homogeneously. However, there are still some octadecyl groups at the surface of the film. We think that the remaining octadecyl groups effect and align the liquid crystal molecules with a slight pretilt angle.

In the case of thermal treatment at 200°C (as shown in Figure 9d), the number of the octadecyl groups decreased further, more than that of at 185°C. And the critical surface tension increases drastically at about this temperature. A few octadecyl groups remained but not enough to tilt the liquid crystal molecules. Consequently, the liquid crystal molecules aligned homogeneously with pretilt 0°.

In the case of thermal treatment at 380°C (as shown in Figure 9e), the number of the octadecyl groups disappeared almost completely. Therefore, the liquid crystal molecules alignment is perfectly homogeneous with pretilt angle 0°.

As we described above, the octadecyl groups have a great effect on causing a pretilt angle. However, we need further examination to discuss the details of the schematic interaction between the octadecyl groups and the liquid crystal molecules interface.

5. CONCLUSIONS

We discovered that the pretilt angle can be controlled by changing the degree of imidization of the LB films to control the number of the long chain alkyl grups.

We have successfully fabricated TN-LCDs without reverse twist and tilt disclinations defect using polyimide alignment films produced by this LB technique.

The pretilt angle is obtained by balancing the homeotropic and the homogeneous alignment forces, which are from the long chain alkyl groups and the main chains of the polyimide, respectively.

A slight pretilt angle, which is needed for TN-LCDs, is achieved since when the effect of the long chain alkyl groups on liquid crystal molecules becomes weak and the effect of the main chains of the polyimide is strengthened.

Acknowledgment

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